SOME ASPECTS OF THE CHEMISTRY OF
4-SUBSTITUTED-1,2,4-TRIAZOLINE-3,5-DIONES

BY

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INTRODUCTION

Triazoline diones are among the most reactive dienophiles known, and their reactivity with various dienes to form Diels-Alder addition products has been widely examined. However, the highly reactive nature of triazoline diones extends to other types of reactions which have not been so thoroughly investigated. The present research was undertaken to extend the knowledge of the thermal and photochemical reactivity of triazoline diones.

In the course of this research several new 4-substituted-1,2,4-triazoline-3,5-diones (the abbreviation TAD will be used at times throughout this thesis) were conveniently synthesized by the oxidation of the corresponding 4-substituted-1,2,4-triazolidine-3,5-diones (these compounds will be referred to by their common name, urazole, throughout this thesis) by dinitrogen tetroxide/nitrogen dioxide. The thermal reactions of triazoline diones with monoolefins containing an allylic hydrogen to form additive-substitution products and their reactions with various substituted styrenes to form 2:1 adducts are discussed.
In addition, the photochemical reactivity of triazoline diones with various hydrogen-donating substrates to yield 1,4-substituted urazoles was explored. Finally, the ability of several of the triazoline diones with alkyl substituents in the 4 position to form nitrogen-backboned polymers when irradiated in inert solvents is discussed.
HISTORICAL

The cyclic diacyl diimide compounds, 4-substituted-1,2,4-triazoline-3,5-diones (2) were first synthesized around the turn of the century by Thiele and later by Stolle. However, the chemistry of these highly reactive compounds was not extensively explored until the beginning of the 1960's. In many ways the chemistry of these diones parallels that of the more extensively investigated diethyl azodicarboxylate, but the former are in many instances much more reactive. A good review with many pertinent references to the chemistry of these and other \( \alpha \)-carbonyl azo compounds appeared in 1966.

All known syntheses of these diones require oxidation of the corresponding urazole 1 as the final step (Equation 1). A variety of reagents are capable of affecting this oxidation.

\[
\text{1} \quad \text{[O]} \quad \text{2}
\]  

(1)
Thiele used lead peroxide in cold dilute sulfuric acid;\(^1\) Stolle oxidized heavy metal salts of the urazole with iodine;\(^2\) Cookson used \(t\)-butyl hypochlorite in acetone;\(^{14}\) and Gillis and Hagerty employed lead tetraacetate in methylene chloride.\(^{15}\) These latter two oxidizing systems had previously been used by Kealy\(^{16}\) and Clement\(^{17,18}\) to oxidize similar cyclic diacyl hydrazides to the corresponding azo products. More recently both bromine\(^{19}\) and fuming nitric acid\(^{10}\) have been reported to affect the urazole oxidation. Manganese dioxide, calcium hypochlorite and N-bromosuccinimide will also oxidize urazoles.\(^{21}\) The last reagent has since been used by Bock to prepare a number of azobisphosphonic acid derivatives.\(^{22}\) Gillis and Izydore have employed both lead tetraacetate and dinitrogen tetroxide in an analogous system to oxidize 4,4-diethylpyrazolidine-3,5-dione (3) to 4,4-diethylpyrazoline-3,5-dione (4).\(^{23}\)
Although several triazoline diones with various 4-substituents have been isolated and characterized, the parent compound \( \mathcal{O} \{ R = H \} \) has not been isolated. Stolle reported preparing the parent dione, but did not isolate it;\(^2\) however, more recently de Amezua and coworkers reported trapping the parent dione with several dienes and characterizing the Diels-Alder adducts formed.\(^2^4\)

Kinetic studies have shown that PhTAD is a more powerful dienophile than tetracyanoethylene,\(^1^9,2^5\) and the reactivity of triazoline diones in this capacity has been extensively investigated. The reactions of PhTAD with cyclopentadiene at \(-78^\circ\) and with butadiene at \(-50^\circ\) are reported to be instantaneous to afford the 1:1 Diels-Alder adducts \(5\) and \(6\), respectively.\(^1^4\) Similar cycloaddition reactions have been reported for triazoline diones with a wide variety of dienes.\(^2^6-3^1\)

\[
\begin{align*}
\text{5} & \quad \text{6}
\end{align*}
\]

Cookson and coworkers have reported that the addition of PhTAD to cycloheptatriene and cyclooctatetraene resulted in the formation of 1:1 adducts \(7\) and \(8\), respectively.\(^3^2\)
However, Evinin and coworkers claim that the same reaction conditions 8 and 9 were isolated in approximately equal amounts from the reaction of PhTAD and cyclooctatetraene. Moreover, if the reaction is run at 25°C in benzene or acetone, 9 is the major product, and only trace amounts of 8 are observed.\textsuperscript{33}

The addition of PhTAD to styrene yields a 2:1 adduct 10 which is the result of two consecutive Diels-Alder additions of PhTAD to styrene.\textsuperscript{32} The reaction of equimolar
amounts of PhTAD with oxonin affords a 1:1 adduct 11 which can react with another mole of PhTAD in a Diels-Alder fashion to produce a 2:1 adduct.\textsuperscript{34} Thermal rearrangement of oxonin yields cis-8,9-dihydrobenzofuran which also forms a 1:1 adduct\textsuperscript{35,36} with PhTAD 12.

Other interesting 1,4-cycloaddition reactions include the addition of PhTAD to tropone, azepine, and diazepine to yield the 1:1 adducts 13, 14, and 15, respectively. However,
the reaction of PhTAD with tropolone is reported to yield the 1,4-substituted urazole 16. 37

\[ \text{13} \]

\[ \text{14} \]

\[ \text{15} \]

\[ \text{16} \]

The reaction of PhTAD with isopyrazoles also leads to the formation of 1:1 Diels-Alder adducts 17. Irradiation of adduct 17 causes elimination of nitrogen to form the corresponding 1,5,7-triazatricyclo[3.1.0.0^{2,6}]octane (18) which can react further with PhTAD to yield a 2:1 adduct 19. 38, 39 Roth and Martin had previously found that PhTAD reacts in a
similar fashion across the central bond of bicyclo[2.1.0]-pentan-5-spiro-cyclopropane to afford a 1:1 adduct.\textsuperscript{40}

The reactions of PhTAD with 1,4-dioxene and indene to yield 1:1 adducts \textsuperscript{21} and \textsuperscript{22} respectively, provide two more examples of thermal 1,2-cycloaddition reactions of triazoline diones.\textsuperscript{41}
Butler and coworkers have reported that PhTAD undergoes copolymerization with ethyl vinyl ether and divinyl ether to afford a polymer which has two likely candidates for repeating units 23 and 24 \((R = CH_2CH_3 \text{ or } CH=CH_2)\). Since the infrared spectra of these copolymers has a strong absorption at 1610 cm\(^{-1}\) which is assigned to the –C=N– chromophore, they believe that repeating unit 23 is predominant. At 25º in methylene chloride the reaction between divinyl ether and PhTAD afforded

\[
25
\]

\[
26
\]

25 in addition to copolymer and when the mixture is heated to 60º this adduct is converted to copolymer. Evidence for involvement of a
dipolar species in the polymerization mechanism was substantiated by trapping the initial dipolar species, in the ethyl vinyl ether and PhTAD system, with acetone to produce the oxadiazine $^{26,42}$.

Cookson and coworkers have used PhTAD to oxidize alcohols to aldehydes or ketones in high yields at room temperature within a few hours. $^{43}$ These reactions were run in dry benzene and phenylurazole is precipitated as one of the products during the reaction. Reactions involving the use of PhTAD as a ligand to certain iridium complexes has also been noted. $^{44}$
RESULTS AND DISCUSSION

Preparation of 4-Substituted-1,2,4-triazoline-3,5-diones

The triazoline diones used in this investigation were easily synthesized by introducing gaseous dinitrogen tetroxide/nitrogen dioxide into a methylene chloride slurry of the appropriate 4-substituted urazole and anhydrous sodium sulfate. The reaction proceeds rapidly with the appearance of the intensely red dione and concomitant disappearance of the urazole. Filtration to remove the sodium sulfate and evaporation at reduced pressure of the methylene chloride quantitatively yields the crystalline red dione which is readily purifiable by sublimation in the dark. This procedure is believed to be superior in convenience, yield, and purity to all previously reported oxidations (see Historical) of urazoles to triazoline diones. Triazoline diones with the following substituents in the 4 position were prepared by this method: methyl, ethyl, n-butyl, t-butyl, cyclohexyl, phenyl, p-nitrophenyl, and p-methoxyphenyl. In the case of p-nitrophenylTAD, the crude material obtained upon evaporation of the solvent showed a propensity to spontaneously
decompose until it had been further purified by sublimation. Once sublimed, this dione is stable for at least 2 weeks if stored in the dark at 0°. Each of these substituted triazoline diones was characterized by its elemental analyses, mmm, infrared, and visible spectra. The infrared spectra for these diones show a characteristic doublet in the carbonyl region with the higher frequency absorption being more intense. The visible spectrum of MeTAD in carbon tetrachloride as shown in Figure 1 exhibits extensive fine structure in the region from 480 to 590 nm. This fine structure is also apparent in the other triazoline diones with alkyl substituents, but to a lesser extent.

Although the unsubstituted triazoline dione was not isolated, introduction of dinitrogen tetroxide/nitrogen dioxide into a slurry of the unsubstituted urazole in 1,4-dioxane resulted in the production of the characteristic red dione color. Also prepared in the study, but not fully characterized, was a bis-dione, 1,6-hexamethyleneTAD from the corresponding bis-urazole.

This is believed to be the first example of an oxidation of a diacylhydrazine to the corresponding azo compound by dinitrogen tetroxide. However, monoacylhydrazines have been shown to yield acylazides upon treatment with dinitrogen
Figure 1. Visible spectrum of $2.05 \times 10^{-3}$ M solution of 4-methyl-1,2,4-triazoline-3,5-dione in carbon tetrachloride.
FIG. 1

\[ \text{ABSORBANCE} \]

\[ \lambda, \text{nm} \]

[Graph showing absorbance vs. wavelength (\(\lambda\)) with peaks at 510, 540, and 600 nm.]
Because dinitrogen tetroxide exists in equilibrium with nitrogen dioxide, one cannot be certain which of the two species is the active reagent. However, several accounts in the literature report oxidations by agency of dinitrogen tetroxide. The claim that dinitrogen tetroxide is the responsible reagent in the nitrosation of amides further implicates this reagent.

A base-promoted cyclization of the appropriate 1-ethoxycarbonyl-4-substituted semicarbazide (29) was employed to prepare the desired 4-substituted urazoles. These 1-ethoxycarbonyl-4-substituted semicarbazides (29) were prepared in quantitative yields by the addition of the appropriate aryl or alkyl isocyanate to ethoxycarbonylhydrazine (28) and the latter compound was prepared by the reaction of diethyl

\[
\begin{align*}
(C_2H_5O)_2C=O & \xrightarrow{N_2H_4 \cdot H_2O} C_2H_5OCNHNH_2 \\
27 & \quad \rightarrow 28 \\
\text{RNCO} & \quad \downarrow \\
1 & \xleftarrow{\text{base}} C_2H_5OCNHNRCNHR \\
\end{align*}
\]
carbonate (27) with hydrazine hydrate. Spectral and analytical data for the previously unreported semicarbazides and urazoles which were prepared in this investigation are in agreement with the proposed structures. The melting points of 4-phenyl, 4-methyl, 4-n-butyl, 4-ethyl and 4-cyclohexyl urazoles agree with those values reported in the literature.1,50,51 The infrared spectra of the urazoles show a characteristic doublet in the carbonyl region; but in contrast to the triazoline diones, the lower frequency absorption is more intense.

In addition to oxidizing the 4-substituted urazoles to triazoline diones, it was observed the dinitrogen tetroxide-nitrogen dioxide also oxidizes 1,4-substituted urazoles to triazoline diones. It was observed that 1-cyclohexyl-4-methylurazole suspended in methylene chloride is oxidized to MeTAD when gaseous dinitrogen tetroxide/nitrogen dioxide is introduced. This is suggested by the appearance of the characteristic red color of the dione and by the fact that the visible spectrum of this red material is identical to that of an authentic sample of MeTAD. The generality of this reaction has been demonstrated by passing gaseous dinitrogen tetroxide/nitrogen dioxide over small solid samples of all
the 1,4-substituted urazoles prepared during this study and noting the appearance of the characteristic red color.

**Reactions with Monoolefins**

Triazoline diones are among the most reactive dienophiles known. For example, red solutions of phenylTAD are decolorized instantaneously at -78° by cyclopentadiene.\(^{14,15}\) For comparison at 20° in 1,4-dioxane, phenylTAD is approximately 140 times more reactive towards 1,4-diphenylbutadiene than is tetracyanoethylene.\(^{19}\)

It has been found that triazoline diones are also extremely reactive towards monoolefins having allylic hydrogens. For example, a methylene chloride solution 0.01 M in MeTAD and 1.0 M in cyclohexene is decolorized within 6 minutes at 25° after mixing. In comparison, diethyl azodicarboxylate, which is recognized as a good dienophile, also reacts in an analogous manner with olefins having allylic hydrogens but far more slowly.\(^{52}\) A comparable solution of this ester and cyclohexene in a degassed sealed tube is incompletely reacted after 6 weeks at 50°. Thus qualitatively, MeTAD is at least sixty thousand times more reactive towards cyclohexene than is diethyl azodicarboxylate. Cookson, Gilani, and Stevens report that when phenylTAD is allowed to
react with cyclohexene in a sealed tube at 175-180° for 3 hours, the expected 1:1 adduct is formed.\textsuperscript{32} In view of the rapid reaction of MeTAD with cyclohexene, these conditions seem extreme.

This Diels-"ene" type reaction results in quantitative formation of a 1:1 adduct of the addition-substitution type first noted by Diels and Alder,\textsuperscript{53,54} and more recently by Thaler and Franzus.\textsuperscript{55} In this study the 1:1 adducts of n-ButTAD with cyclohexene and 2,3-dimethyl-2-butene and the 1:1 adducts of MeTAD with cyclohexene, cyclopentene, 2,3-dimethyl-2-butene, \textit{trans}-2-butene, and \textit{cis}-2-butene were prepared by the simple addition of the olefin to a methylene chloride solution of the triazoline dione. The reaction of MeTAD with either \textit{cis}-2-butene or \textit{trans}-2-butene affords the same 1:1 adduct, 1-(3-butene-2-yl)-4-methylurazole (30), as was determined by their identical elemental analyses, infrared and nmr spectra, and an undepressed mixed melting point. The other 1:1 adducts, 1-(2,3-dimethyl-3-butene-2-yl)-4-methylurazole (31), 1-(2,3-dimethyl-3-butene-2-yl)-4-n-butylurazole (32), 1-(2-cyclohexen-1-yl)-4-methylurazole (33), 1-(2-cyclopenten-1-yl)-4-methylurazole (34), and 1-(2-cyclohexen-1-yl)-4-n-butylurazole (35) all have the correct elemental composition and have infrared and nmr spectra consistent with the
30. $R^1 = \text{Me}; R^2 = R^3 = \text{H}$  
31. $R^1 = \text{Me}; R^2 = R^3 = \text{Me}$  
32. $R^1 = n\text{-Bu}; R^2 = R^3 = \text{Me}$  
33. $R^1 = \text{Me}; n = 3$  
34. $R^1 = \text{Me}; n = 2$  
35. $R^1 = n\text{-Bu}; n = 3$

suggested structures. The infrared spectra of all these adducts show a characteristic doublet in the carbonyl region, with the lower frequency absorption being more intense.

The structures of the adducts 30, 31, and 32, arising from the aliphatic olefins, indicate that a shift in the position of the double bond has occurred; however, one cannot conclude from the structures of the alicyclic olefin addition products 33, 34, and 35 whether or not a migration of the double bond has occurred. Franzus and Thaler have reported that in the reaction of monoolefins with diethyl azodicarboxylate, the aliphatic olefins react by a concerted mechanism with a six-membered-ring transition state, 36, while the alicyclic olefins react primarily by a radical pathway of proton abstraction followed by radical recombination.
Methods similar to those used by these investigators may prove appropriate in ascertaining whether or not the mechanism above obtains in the reactions of triazoline diones with aliphatic and alicyclic monoolefins. In addition, studies of the effect of various 4 substituents upon reactivity toward monoolefins should provide further information concerning the nature of the mechanism of this reaction.

Because of the facile nature of this reaction, one might utilize triazoline diones as derivatizing reagents for low-melting monoolefins. Another application of this reaction might be the formation of an adduct of a triazoline dione containing a heavy atom in the 4 substituent, such as 4-(p-bromophenyl)-1,2,4-triazoline-3,5-dione, with an olefinic compound otherwise unsuitable to X-ray analysis. Hopefully the adduct would be sufficiently crystalline to be amenable to the X-ray technique.

Reactions with Substituted Styrenes

A preliminary examination shows that triazoline diones are also very reactive toward compounds containing a styrene
moiety and provides another example of triazole diones reacting in an additive-substitution fashion. For instance, when MeTAD was allowed to react with styrene, \(\alpha\)-methylstyrene, and trans-stilbene, 2:1 adducts 37, 38, and 39 of MeTAD to substrate were isolated.

\[
\begin{align*}
37, & \quad R^1 = R^2 = H \\
38, & \quad R^1 = \text{Me}; \quad R^2 = H \\
39, & \quad R^1 = \text{H}; \quad R^2 = \text{Ph}
\end{align*}
\]

The mechanism for the formation of these adducts presumably involves an intermediate 1:1 adduct 40 which results from a Diels-Alder addition of MeTAD to the styrene compound. The intermediate then reacts with another molecule of MeTAD.
in a Diels-"ene" manner by abstraction of the allylic hydrogen on the bridgehead and addition with a shift in the double bond causing re-aromatization. The nmr and infrared spectral data and the elemental analyses of the 2:1 adducts 37, 38, and 39 are consistent with the proposed structures.

Although diethyl azodicarboxylate is known to undergo similar reactions with substituted styrenes, these reactions are much slower than those of MeTAD with substituted styrenes. It is reported that diethyl azodicarboxylate fails to react with 2,6-dichlorostyrene. Because of its greater reactivity, it was thought that MeTAD might react with 2,6-dichlorostyrene with the chlorine substituent blocking the Diels-"ene" addition to the intermediate. Possibly the intermediate would then react with a second molecule of MeTAD by a Diels-Alder addition. However, the only product isolated from the reaction of MeTAD with 2,6-dichlorostyrene was a 1:1 adduct 41. Perhaps the initial intermediate resulting from a Diels-Alder addition loses hydrogen chloride by a 1,4
elimination, and then hydrogen chloride adds across the newly-formed double bond. The nmr and infrared spectral data and elemental analysis are consistent with the proposed structure.

Photochemical Reactions of 4-Substituted-1,2,4-triazoline-3,5-diones with Hydrogen-donating Substrates

An investigation of the photochemistry of triazoline diones indicates that they react with various hydrogen-donating substrates to form 1:1 adducts (Equation 2). These products are analogous in structure to the olefin-dione adducts described earlier, except that they lack a double bond in the 1 substituent. Diethyl azodicarboxylate also reacts photochemically with hydrogen-donating substrates to product 1-substituted hydrazines (Equation 3).\[^{59}\]

\[
\begin{align*}
\text{EtOCN-NCOEt} + R^1H & \xrightarrow{hv} \text{EtOCNHNR} + \text{COEt} \\
2 + R^1H & \xrightarrow{hv} \end{align*}
\]
Irradiation of cyclohexane solutions of n-BuTAD in a Rayonet photochemical reactor using the low-pressure mercury 2537 Å lamps afforded in 19% yield 1-cyclohexyl-4-n-butylurazole (42). In addition to this product about twice as much of another, unstable, substance was isolated but not identified. The nmr spectrum of this unstable liquid contains absorptions attributable to both the n-butyl and cyclohexyl moieties. When the irradiation was carried out using a 500-W tungsten filament General Electric lamp, the reaction afforded a 92% yield of 42. The nmr spectrum of adduct 42 in carbon tetrachloride exhibits a broad multiplet at $\tau 6.12$ overlapping with a broad triplet at $\tau 6.50$ for the three protons $\alpha$ to nitrogen, and a complex multiplet centered at $\tau 8.53$ for remaining seventeen n-butyl and cyclohexyl protons. The infrared spectrum in carbon tetrachloride contains two broad absorptions at 3150 and 3060 cm$^{-1}$ assigned to N-H stretching and a carbonyl doublet at 1756 and 1688 cm$^{-1}$, the latter being the more intense. The analytical
data is also consistent with the assigned structure. Confirmation of the structure of the photoproduct, 42, was obtained by an independent synthesis of this compound. The olefin-dione adduct, 1-(2-cyclohexen-1-yl)-n-buty lurazole (35) reported earlier, was hydrogenated to photoproduct 42 using palladium on charcoal as a catalyst. The infrared and nmr spectra of the reduction product are identical to that of the photoproduct, and the mixed melting point is undepressed.

Diethyl azodicarboxylate also reacts photochemically with ethers by abstraction of the hydrogen at the α-carbon followed by addition resulting again in a 1-substituted hydrazine. It has been found that this is also the case with MeTAD when it is irradiated in a Rayonet photochemical reactor using the 2537 Å lamps in dioxane. This reaction afforded 1-(1,4-dioxan-2-yl)-4-methylurazole (43) in 63%

![Image of structure 43]

yield. The nmr spectrum of photoproduct 43 in trifluoroacetic acid displays a triplet at σ 4.26 assigned to the α nitrogen proton, and a multiplet at σ 5.79 assigned to the
other six dioxanyl protons, and a singlet at \( \tau 6.71 \) assigned to the nitrogen methyl protons. The infrared spectrum shows a broad absorption centered at 3050 cm\(^{-1} \) assigned to N-H stretching and a carbonyl doublet at 1786 and 1705 cm\(^{-1} \), the latter being more intense. The analytical data for photo-product 43 is also consistent with the assigned structure. Gustorf, White, Kim, Hess, and Leitich have reported the synthesis of 1-(1,4-dioxan-2-yl)-4-phenylurazole by a different route. In this case the 1,2-cycloaddition product 2l of phenylTAD and dioxene was hydrogenated using Raney nickel as a catalyst to afford the 1,4-substituted urazole.

Cookson and coworkers have reported that the photochemical 1:1 adducts resulting from the addition of diethyl azodicarboxylate at the \( \alpha \)-carbon of ethers are easily hydrolyzed in hot water to diethyl hydrazodicarboxylate, the expected alcohol, and carbonyl compound. Triazoline diones may find similar application in the cleavage of ethers and ketals which are difficult to hydrolyze.

The photochemical reactions of various triazoline diones with cumene constitute further examples of the ability of these diones to react with hydrogen donating substrates. Irradiation with a 500-W General Electric projector lamp of
cumene solutions of MeTAD, p-methoxyphenylTAD, or phenylTAD results in the formation of 1-cumyl-4-methylurazole (44), 1-cumyl-4-(p-methoxyphenyl)-urazole (45) and 1-cumyl-4-phenylurazole (46), respectively. The reaction of MeTAD

\[ \text{MeTAD} \]

with cumene was observed to be faster than that of phenylTAD which in turn was faster than that of p-methoxyphenylTAD. The postulated pathway for this reaction is abstraction of the tertiary proton of cumene by excited triazolene dione followed by radical recombination. The nmr spectrum of the unpurified product of the reaction of MeTAD with cumene shows a doublet at \( \tau 8.76, J = 7.0 \) Hz attributable to the protons of the C-methyl group in a secondary product, 1-(2-phenyl-propyl)-4-methylurazole (47), resulting from the abstraction
of a primary proton from cumene followed by recombination, although this product was not present after recrystallization from ethanol and water.

The nmr spectrum of compound 44 in dimethyl sulfoxide-d$_6$ shows a multiplet for five aromatic protons at $\tau$ 2.68, a singlet for three methyl protons $\alpha$ to nitrogen at $\tau$ 7.15, and a singlet for six protons of the C-methyl groups at $\tau$ 8.29. The nmr spectrum for compound 45 in dimethyl sulfoxide-d$_6$ shows overlapping multiplets for nine aromatic protons at $\tau$ 2.90, a singlet for three methoxyl protons at $\tau$ 6.28, and a singlet for six protons of the C-methyl groups at $\tau$ 8.24. The nmr spectrum of compound 46 in dimethyl sulfoxide-d$_6$ shows a multiplet for ten aromatic protons centered at $\tau$ 2.66 and a singlet for six protons of the C-methyl groups at $\tau$ 8.23. The infrared spectra of compounds 44, 45 and 46 in Nujol all show absorption in the N-H stretching region and the usual doublet in the carbonyl region with the lower frequency absorption being the more intense. The analytical data for compounds 44, 45 and 46 are also consistent with the assigned structure. The 1,4-substituted urazole 44 was also isolated from the much slower thermal reaction of MeTAD with cumene at room temperature.
Photopolymerization of 4-Alkyl-1,2,4-triazoline-3,5-diones

A kinetics study of the photochemical reaction of MeTAD with cumene, in which the rate of disappearance of MeTAD in a large excess of cumene was monitored by the decrease in the visible absorption of MeTAD, indicated that the reaction did not follow the expected pseudo-first-order rate law. This discrepancy involved a partial regeneration of the MeTAD which had disappeared during the irradiation period. For example, after 3 minutes of irradiation of a 6.95 x 10^{-3} M solution of MeTAD in cumene, the visible absorption at 538.5 nm indicated that approximately 31.5% of the MeTAD present initially had disappeared, but after about 10 minutes in the dark 19.7% of the originally reacted MeTAD had regenerated with an estimated half-life of ca. 2 minutes. When a correction for this regeneration phenomenon was made for each period of the irradiation, a pseudo-first-order rate law was more closely obeyed.

In order to study this regeneration phenomenon further, a suitable solvent was needed. An ideal solvent must meet the following criteria: the triazoline dione and photoproduct must, of course, show the necessary solubility; it must give a rapid rate of disappearance of alkylTAD coupled
with a slow rate of regeneration of alkylTAD; and it should be photochemically and thermally inert to the dione at least in time needed to photobleach and regenerate the dione. Although the list of solvents which show at least some regeneration phenomenon is extensive, many failed to fill all of the above criteria. For instance, in aromatic solvents such as benzene alkylTAD's prove very resistant to photobleaching; and, although irradiation will cause partial disappearance of the diones, regeneration is rapid. Thus, although 40% of the t-BuTAD in a dilute benzene solution disappeared after 20 minutes of irradiation, within 8 minutes after irradiation ceases, 96% of the dione was regenerated. In aromatic solvents with electron-withdrawing substituents, alkylTAD's are somewhat less resistant to photobleaching; a dilute solution of n-BuTAD in hexafluorobenzene was irradiated to colorlessness in 1 hour, and approximately 74% had regenerated within 25 hours; however, turbidity of the photobleached solution indicated insolubility of photo-product. Other solvents such as acetone, dimethyl carbonate, and methyl acetates allow rapid disappearance of alkylTAD's, but, also, rapid and incomplete regeneration, presumably indicating formation of another product via hydrogen abstraction from solvent.
The most suitable solvents examined in this study were alkyl halides, such as carbon tetrachloride, methylene chloride, and chloroform. For example, a dilute solution of \( n \)-BuTAD in carbon tetrachloride was irradiated to colorlessness within 5 minutes and was 73% regenerated after 300 hours. For a comparison of the relative rates of regeneration of \( n \)-BuTAD in carbon tetrachloride, methylene chloride, and hexafluorobenzene as monitored by visible spectroscopy see Figure 2.

The initial evidence that the photobleaching and regeneration phenomenon involved a polymerization of the triazoline dione was obtained by experiments with the vapor pressure osmometer indicating large molecular weights for the species present in the photobleached solutions. For example, if a 0.3 M solution of \( n \)-BuTAD is irradiated using a visible light source (150-W quartz-iodine tungsten lamp) for 8 minutes there is obtained a colorless solution of photo-polymer having an observed (vapor pressure osmometer with 25\(^{\circ}\) thermostat) average molecular weight of 4200 initially. This implies that the average polymer molecule contains at least twenty monomer units. This value may be low owing to the sensitivity of the osmometric technique toward non-polymeric impurities and also because of the several minutes
Figure 2. Comparison of plots of % regeneration of n-BuTAD from photopolymers formed in the same solvents as a function of time. Percent regeneration is defined as the ratio of visible absorbance of n-BuTAD at a given time to the visible absorbance of n-BuTAD before irradiation.
time lapse in obtaining the initial measurement. As can be seen in Figure 3, which compares the decrease in the molecular weight of the \( \text{n-BuTAD} \) photopolymer as a function of time at 37\(^\circ\) and 25\(^\circ\) as monitored by vapor pressure osmometry, the initial portions of the curves show a very rapid decrease in molecular weight, so the several minutes needed to ready the photobleached sample for the measurements probably results in substantial reduction of initial molecular weight of photopolymer. Visible spectroscopy indicated that about 4\% of the red monomer is regenerated at 27\(^\circ\) within 30 minutes after completion of the photopolymerization of the 0.3 M solution of \( \text{n-BuTAD} \) in carbon tetrachloride. At the same time the observed molecular has dropped to about 2700 at 25\(^\circ\).

Low-temperature evaporation of the solvent from a freshly bleached 0.3 M solution of \( \text{n-BuTAD} \) in carbon tetrachloride provided a slightly pink glass. The analytical data for this glass gave carbon and hydrogen analyses in accord with that calculated for a monomer unit, although the analyses did show the presence of 1.44\% of chlorine, this is believed to be due to residual solvent rather than solvent participation in the polymerization. Although the polymeric glass was stored for about a year at 14\(^\circ\) in the dark, no appreciable monomer regeneration was evident. However, when the stored
Figure 3. Comparison of plots of the ratio of the molecular weight observed by vapor osmometry to the molecular weight of n-BuTAD as a function of time at 25° and 37°.
polymer was redissolved in methylene chloride, regeneration of the monomer was detected.

A priori, only four types of repeating units, 48, 49, 50, and 51 would seem plausible to occur in the structure of the labile n-BuTAD photopolymer. The ring-opened structure 51 would be expected to cause the polymer to be yellow owing to the presence of the n-π* absorption of the azodicarbonyl chromophore. Typical azodicarbonyl compounds have n-π*
absorption bands that occur in the 410-475 nm region with ε ranging from 37 to 56. The visible spectrum of the photo-polymer indicates that no extraneous absorption is observed in this region and it can be estimated, using the values above, that there is less than 4% of this type of chromophore present in the photopolymer. Therefore the ring-opened structure 51 is eliminated from serious consideration as a repeating unit contributing to the structure of the polymer.

Of the remaining three possible repeating units, 48, 49, and 50, only 50, representing a nitrogen-backboned polymer, is consistent with infrared spectral data. In connection with this infrared study, three model compounds were prepared. Diazomethane treatment of 1-cyclohexyl-4-methylurazole (52), which was prepared by the hydrogenation of 1-(2-cyclohexen-1-yl)-4-methylurazole (33), using palladium on charcoal as a catalyst, afforded a 1:3 mixture of chromatographically separable O-methyl and N-methyl derivatives, 1-cyclohexyl-3-methoxy-4-methylurazole (53) and 1-cyclohexyl-2,4-dimethylurazole (54), respectively. Compounds 52, 53, and 54 each have elemental compositions and nmr and infrared spectral properties in accordance with the assigned structure. In particular, the infrared spectrum of 53 shows only a single sharp carbonyl band at 1707 cm⁻¹
and two intense absorption bands at 1513 and 1605 cm\(^{-1}\) which are associated with the imidate-like functionality and which are absent from the infrared spectra of urazoles 52 and 54. Since the infrared spectrum (IR-10) of the photopolymer shows a broad carbonyl absorption centered at 1768 cm\(^{-1}\), but no absorption near the 1513 and 1605 cm\(^{-1}\) region which might be attributed to the imidate-like groups present in repeating units 48 and 49, it is clear that these two types of units occur seldom, if ever, in the polymer. Consequently, 50 is the only remaining plausible repeating unit; and, therefore, this photopolymer apparently has a nitrogen backbone as its principle linkage. Compatible with this interpretation is the observation that the integrated intensity of the polymer's carbonyl absorption band (relative area 1.81) indicated, when compared to similar measurements on model compounds 52, 53 and 54 with equivalent concentrations (relative areas 2.29, 1.01, and 2.00, respectively), that essentially all the carbonyl groups of the monomer are retained upon poly-
merization. Although similar measurements of the carbonyl intensity of the monomer, n-BuTAD, show a relative area of 1.51 for an equivalent concentration, the monomer is not considered a good model for the polymer because of the conjugative effect of the nitrogen-nitrogen double bond.

Further chemical and spectral data support the proposed structure of the photopolymer. As previously mentioned, a carbon tetrachloride solution of the n-BuTAD photopolymer slowly regenerates a major portion of the red monomer after several days. However, a comparable amount of regeneration takes place within several minutes after an addition of a small amount of pyridine, a mild base, to a freshly photo-bleached solution of n-BuTAD in carbon tetrachloride. For example, 30 minutes after irradiation of a solution of n-BuTAD photopolymer in carbon tetrachloride, 11% of the n-BuTAD had regenerated as monitored by visible spectroscopy; however, a comparable solution of photopolymer which had been treated with pyridine showed that 70% of n-BuTAD had regenerated after the same amount of time. This base-catalyzed depolymerization strongly suggests that the polymer chain is terminated with hydrogen (50, Y = H). Thus, if an acidic terminal hydrogen is removed by base producing an anion, then this anion could subsequently (or concomitantly) eliminate
a monomer unit. Schenck and Formanek have reported a reaction which can be considered an analogy for this base-catalyzed depolymerization. Besides pinacol, these workers isolated a tetracarbethoxytetrazine 55 from the irradiation of diethyl azodicarboxylate in iso-propyl alcohol. Upon treatment with ammonia this tetrazine, 55, having terminal hydrogens, produces azodicarbonamide (56) and diethyl hydra
dodicarboxylate (57) (Equation 4). In addition, above 80° this tetrazine, 55, undergoes a reversible radical dissociation (Equation 5), and above 150° disproportionates to afford diethyl azodicarboxylate and 57 (Equation 6). 59

\[
\text{EtO}_2\text{C(NHN=N=NHCO}_2\text{Et} \xrightarrow{\text{NH}_3} \text{NH}_2\text{C(N=NCNH}_2 \xrightarrow{} \text{EtO}_2\text{C(NHNHC}_2\text{Et}}
\]

55 56 57

(Eq. 4)

\[
55 \xrightarrow{80^\circ} 2 \text{EtO}_2\text{C(NHNCO}_2\text{Et}
\]

(Eq. 5)

\[
55 \xrightarrow{150^\circ} \text{EtO}_2\text{CN=NCO}_2\text{Et} + 57
\]

(Eq. 6)
That the n-BuTAD photopolymer is terminated with hydrogens is further supported by infrared and nmr spectral data. A weak broad absorption observed at 3220 cm\(^{-1}\) in the infrared spectrum and a broad peak at \(\tau 2.65\) in the 220 MHz nmr spectrum (NMR-10) of the photopolymer are attributed to terminal N-H. Additionally, the 220 MHz nmr spectrum of the polymer exhibits four intense broad featureless bands centered at \(\tau 8.98, 8.54, 8.29,\) and 6.34, respectively, which can be assigned to the four types of protons present in the \(n\)-butyl substituents. Besides the broad N-H and carbonyl absorptions in the infrared spectrum (IR-10) of the photopolymer, the spectrum is generally comprised of broad featureless absorptions indicative of a polymer.

Since treatment of urazole 52 with diazomethane afforded methylated products 53 and 54, it was anticipated that similar treatment of the hydrogen terminated photopolymer would methylate the ends and would result in improved stability for the photopolymer. Diazomethane treatment of a freshly photobleached solution of \(n\)-BuTAD in carbon tetrachloride (with subsequent removal of the excess reagent) afforded a polymer which was not only stable towards pyridine, but was also significantly more stable towards thermal depolymerization. For example, after about two days at 27\(^\circ\), a carbon tetra-
chloride solution of the methylated polymer had regenerated only 8.2% of the red monomer, whereas a similar solution of the untreated photopolymer had regenerated approximately 47% of the red monomer. For comparison of the regeneration of red monomer as monitored by visible spectroscopy of the methyl and hydrogen terminated polymers, see Figure 4. The 220 MHz nmr spectrum (NMR-11) of the methylated polymer, in addition to the expected four larger broad resonances of the n-butyl substituents, shows two smaller, similarly sized, resonances at τ 6.97 and 6.08 attributable to N-methyl and O-methyl end groups, respectively. The infrared spectrum (IR-11) of the methyl-capped polymer shows no absorption in the N-H stretching region, but two weak broad bands at 1610 and 1495 cm$^{-1}$, which are not present in the infrared spectrum of the unmethylated polymer. Since strong bands appear at 1605 and 1513 cm$^{-1}$ in the infrared spectrum of the O-methylated urazole, 53, it seems clear that partial O-methylation of the hydrogen terminated photopolymer has given rise to these new bands. By assuming that the imidate-like group which arises on O-methylation of the polymer displays infrared bands of intensity comparable to that which would be shown by the similar functionalities present in polymer units, 48 and 49, then one can roughly estimate a maximum fre-
Figure 4. Comparison of plots of % regeneration of \( n \)-BuTAD in carbon tetrachloride as a function of time from the hydrogen-terminated photopolymer and the methyl terminated polymer (photopolymer treated with diazomethane). Percent regeneration is defined as the ratio of visible absorbance of \( n \)-BuTAD at a given time to the visible absorbance of \( n \)-BuTAD before irradiation.
quency of occurrence of repeating units 48 and 49 in the polymer. As previously mentioned, the average polymer contains at least twenty monomer units and, upon diazomethane treatment, undergoes about equal amounts of N- and O-methylation at the two ends. Since O-methylation is readily detectable by infrared, it may be seen that one imidate-like group in forty units would be detected. Therefore, the estimate is that the frequency of occurrence of repeating units 48 and 49 is less than 2.5%.

Although the stability of the methylated polymer is greatly enhanced, as noted, some regeneration does occur. This suggests that there are at least two modes of depolymerization. One pathway suggested by the base-catalyzed depolymerization study is the removal of a terminal proton and subsequent (or concomitant) elimination of a monomer unit from the resulting anionic polymeric species. In the absence of added base, perhaps another polymer unit can act as a proton acceptor to produce a similar anionic polymer species which can eliminate a monomer unit. Since this pathway is not available to the methylated polymer, depolymerization may occur through nitrogen-nitrogen scission, and regeneration take place by elimination of a monomer unit from the radical-terminated polymer species. Both pathways, of
course, could be taking place in the case of the unmethylated photopolymer. As previously mentioned, the vapor pressure osmometry molecular weight data indicate a rapid decrease in the molecular weight of the polymer within the first several minutes followed by a leveling-off in the rate of decrease. Since there is no corresponding rapid initial rate of reappearance of red monomer as monitored by visible spectroscopy, this suggests that nitrogen-nitrogen bond scission accounts for this initial decrease in molecular weight. The presence of a free radical species in the regenerating polymer solution is substantiated by chemical and spectral data. For instance, if several drops of a solution of diphenylpicrylhydrazyl, a known radical indicator, are added to a freshly photobleached solution of n-BuTAD in carbon tetrachloride, the characteristic violet color is instantly rendered colorless. Also, a complex esr spectrum of a similar solution shows at least a 20-lined resonance which is not readily interpretable.

It is interesting to note, in connection with the diazomethane treatment of the photopolymer, that diazomethane reacts with n-BuTAD to produce a copolymer which in some respects is similar to the methylated photopolymer. The 220 MHz nmr spectrum (NMR-12) shows four broad featureless bands
at $\tau$ 6.44, 8.43, 8.71, and 9.02 attributable to the $n$-butyl groups, two smaller similarly sized resonances at $\tau$ 6.08 and 7.00 attributable to O- and N-methylated end groups respectively, and, in addition to these, a very broad resonance centered at $\tau$ 4.20 which could be attributable to the methylene protons adjacent to two nitrogens and one nitrogen and one oxygen in the proposed basic repeating units, 58 and 59. The infrared spectrum (IR-12) of this polymer shows the usual carbonyl doublet at 1775 and 1712 cm$^{-1}$ with the lower frequency band being more intense, plus absorptions at 1601 and 1495 cm$^{-1}$ associated with the imidate-like functionality. Finally, the vapor pressure osmometric data indicate an average molecular weight of about 3400. Attempts to initiate polymerization of $n$-BuTAD with 2,2'-azobis-(2-methylpropionitrile), a known polymer initiator, were not successful.
The rate of regeneration of monomer appears to be solvent dependent. For instance, when a 0.3 M solution of n-BuTAD in carbon tetrachloride is irradiated to colorlessness, then the solvent removed at reduced pressure from a one milliliter aliquot of this solution and the residue dissolved in enough methylene chloride to bring the concentration to $6 \times 10^{-3}$ M (based on monomer), the regeneration is found to be much more rapid than a similar solution of n-BuTAD photopolymer in carbon tetrachloride. For example, after about one day 69% of the monomer in the methylene chloride solution was regenerated, but in the carbon tetrachloride solution only 34% of monomer had reappeared, as monitored by visible spectroscopy. For comparison of the rate of regeneration in these two solvents see Figure 5. The rate of regeneration in methylene chloride from the photopolymer from irradiation in carbon tetrachloride is similar to that of the photopolymer from irradiation in methylene chloride except that the former regenerates about 74% of original monomer, while the latter only about 50%. The value of 50% is believed to be due to impurities present in methylene chloride, since successive irradiations allowing regeneration to be completed after each irradiation of a MeTAD in a methylene chloride solution resulted in about 90% regeneration of monomer after
Figure 5. Comparison of plots of % regeneration of $\text{n-BuTAD}$ in carbon tetrachloride and methylene chloride from photopolymerization of $\text{n-BuTAD}$ in carbon tetrachloride as a function of time. Percent regeneration is defined as the ratio of visible absorbance of $\text{n-BuTAD}$ at a given time to the visible absorbance of $\text{n-BuTAD}$ before irradiation.
the third irradiation, presumably through exhaustion of impurities present in the original solution.

In connection with these two solvents, carbon tetrachloride and methylene chloride, it was observed that oxygen inhibited photopolymerization of triazoline dione in the former, but did not seem to influence this reaction in the case of the latter. For example, 2 ml of a 0.1 M solution of n-BuTAD in carbon tetrachloride which was flushed with a stream of nitrogen 5 minutes prior to and during irradiation was rendered colorless within 6 minutes, but a similar solution not flushed with nitrogen took 45 minutes to become colorless. Nevertheless, vapor pressure osmometry data on a solution of n-BuTAD in carbon tetrachloride photobleached in the presence of oxygen indicated formation of a photopolymer of an initial average molecular weight of about 2500.

Since n-BuTAD undergoes ready photoreaction with hydrogen donors such as cyclohexane, it may be that polymerization is initiated by hydrogen abstraction of the excited state of n-BuTAD from the n-butyl group of another molecule of the dione to afford a repeating unit such as 60. This type of reaction may explain the incomplete regeneration of monomer from the polymer. Although the hydrogen α to the nitrogen would presumably be the most reactive, that α-
hydrogens are not necessarily required is demonstrated by the observation that \( \text{t-BuTAD} \) also undergoes photopolymerization. A synthesis of a perdeuterated alkylTAD would provide corroboration of this postulate by the observation of a shift in the N-H stretching band to the N-D stretching region in the infrared spectrum of the photopolymer and would help clarify any question about solvent participation in the photopolymerization reaction.

Whereas both 4-alkyl and 4-aryl-1,2,4-triazoline-3,5-diones undergo photoreactions with hydrogen donors, it has been observed that only the former undergoes ready photopolymerization and then only, as previously mentioned, in certain solvents. Typically, if a 4-alkyl-1,2,4-triazoline-3,5-dione will fluoresce in a solvent, it will undergo photopolymerization in that solvent. A notable exception to this rule is the observation that, although a solution of MeTAD in acetonitrile shows fluorescence, this solution is resistant to photopolymerization. When acetonitrile is added
in small amounts to photobleached solutions of MeTAD in methylene chloride, no dramatic acceleration of regeneration is observed; perhaps acetonitrile as solvent is basic enough and in high enough concentration that base-catalyzed depolymerization competes too strongly with photopolymerization for the latter to be observed.

As discussed earlier, benzene and most other aromatic solvents quench the fluorescence (presumably by reducing the lifetime of the excited singlet) and inhibit polymerization of alkylTAD's. Even small amounts of benzene added to solutions of MeTAD in methylene chloride inhibit photopolymerization. Possibly the arylTAD's, which do not fluoresce well, undergo "self-quenching." Since emission is not quenched in aromatic solvents having strong electron-withdrawing substituents such as hexafluorobenzene and trifluoromethylbenzene, and photopolymerization has been shown to take place in hexafluorobenzene, it would be interesting to examine the photochemical properties of 4-(p-trifluoromethylphenyl)-1,2,4-triazoline-3,5-diones, which presumably might not undergo "self-quenching", but contains no easily abstractable hydrogens in the 4 substituent.
EXPERIMENTAL

Nuclear magnetic resonance spectra were determined on Varian Associates A-60, A-50A, A-55/60, HA-100, or HR-100 spectrometers, and chemical shifts are expressed in $\tau$ units relative to tetramethylsilane (TMS) as an internal standard ($\tau = 10.00$). The infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer or a Perkin-Elmer Model 137 Infracord spectrophotometer. In the discussions of the infrared spectral data the abbreviations vs, s, m, and w stand for very strong, strong, medium, and weak, respectively. The visible spectra were run on a Cary 14 recording spectrophotometer or a Perkin-Elmer 202 ultraviolet-visible spectrophotometer. Microanalyses were conducted by Mr. J. Nemeth and his associates at the University of Illinois Microanalytical Laboratory. Melting points were determined on a Buchi Melting-Point Apparatus or Kofler block and are uncorrected, as are boiling points. Molecular weights were determined on a Mechrolab Vapor Pressure Osmometer, Model 301A. Reagent grade chemicals were used without further purification, unless otherwise specified.
Preparation of Ethoxycarbonylhydrazine (28). This compound was prepared from hydrazine hydrate (85%) and diethylcarbonate (27) according to the procedure of Diels. 49

Preparation of 4-Substituted-1-ethoxycarbonyl Semicarbazides (29). The semicarbazides were synthesized by the addition of appropriate aryl or alkyl isocyanates to ethoxycarbonylhydrazine (28) by the method of G. Zinner and W. Deucker. 48

Preparation of 4-Substituted Urazoles (1). These compounds were prepared by the cyclization of the corresponding 1-ethoxycarbonyl-4-substituted semicarbazide (29) with sodium hydroxide in water by the method of Zinner and Deucker 48 or by a slight modification using sodium methoxide in ethanol.

Preparation of 4-Substituted-1,2,4-triazoline-3,5-diones (2)

A. MethylTAD. To a slurry of 0.933 g (8.25 mmol) of 4-methylurazole and 10 g of anhydrous sodium sulfate in 50 ml of methylene chloride at 0°C, was passed a steady stream of dinitrogen tetroxide/nitrogen dioxide (Matheson Co.) through a narrow tube until it appeared that all the urazole had reacted. The resulting dark red solution was filtered to remove the sodium sulfate and the red filtrate evaporated to dryness at reduced pressure in the dark to afford a red
crystalline solid. After sublimation (0.01 mm, 50°, in the
dark) of this solid, 0.747 g (6.61 mmol, 81%) of pure MeTAD,
mp 98.0-98.5°, was isolated.

The nmr spectrum (CDCl₃) displays a sharp singlet at
τ 6.76 (NCH₃). The infrared spectrum shows absorption at
1784, 1738 (vs, C=O), and 1530 cm⁻¹ (w, N=N). The visible
spectrum (CCl₄) contains absorptions at 503 (ε 68), 515 (ε
121), 527 (ε 176), 543 (ε 230), 554 (ε 208) and 573 nm
(ε 215). The UV spectrum (CH₂Cl₂) show an absorption at
289 nm (ε 2,150).

Anal. Calcd for C₁₂H₂₁N₃O₂:  C, 60.23; H, 8.84.
    Found:  C, 60.04; H, 8.74.

B. CyclohexylTAD, mp 93.5-94.5°, was prepared in a
manner similar to that used for MeTAD in 87% yield after
two sublimations (0.01 mm, 40°). The nmr spectrum (CCl₄)
displays a very broad peak at τ 6.12 (1 H, NCH) and a
complex multiplet at τ 8.28 (10 H, C₅H₁₀). The infrared
spectrum (CCl₄) shows absorption at 1756 (vs, C=O) and 1515
(w, N=N). The visible spectrum (C₆H₁₂) shows absorptions at
528 (ε 153), 545 (ε 205), and 572 nm (ε 172).

    Found:  C, 53.03; H, 6.13.
C. *n*-ButylTAD, mp 44.0-44.5°, was prepared in a manner similar to that used for MeTAD in 71% yield after two sublimations (0.01 mm, 35°). The 220 MHz nmr spectrum (CCl₄, NMR-1) displays a 3-lined multiplet at τ 6.26 (2 H, NCH₂), a 5-lined multiplet at τ 8.25 (2 H, CH₂), a 6-lined multiplet at τ 8.59 (2 H, CH₂), and a 3-lined multiplet at τ 8.97 (3 H, CH₃). The infrared spectrum (CCl₄, IR-1) shows bands at 1781, 1754 (vs, C=O), and 1520 cm⁻¹ (w, N=N). The visible spectrum (CCl₄) shows absorptions at 528 (ε 168), 545 (ε 227), 553 (ε 198), and 574 nm (ε 206).

**Anal.** Calcd for C₆H₉N₃O₂: C, 46.45; H, 5.85.

Found: C, 46.60; H, 5.79.

D. *t*-ButylTAD, mp 132.5-134° with slight decomposition, was prepared in a manner similar to that used for MeTAD in 79% yield after two sublimations (0.01 mm, 40°). The nmr spectrum (CDCl₃) exhibits a singlet at τ 8.34 (C(CH₃)₃). The infrared spectrum (CH₂ClCH₂Cl) shows absorption at 1780, 1754 (vs, C=O), and 1523 cm⁻¹ (w, N=N). The visible spectrum (CCl₄) shows absorptions at 545 (ε 204) and 574 nm (ε 165).

**Anal.** Calcd for C₆H₉N₃O₂: C, 46.45; H, 5.85.

Found: C, 46.58; H, 5.81.

E. EthylTAD, mp 47.5-50.0°, was prepared in a manner similar to that used for MeTAD and sublimed (0.1 mm, 50°)
three times. The nmr spectrum (CDCl₃) exhibits a quartet at \( \tau 6.23 \) (2 H, \( J = 7.5 \) Hz, NH₂) and a triplet at \( \tau 8.65 \) (3 H, \( J = 7.5 \) Hz, CH₃). The infrared spectrum (CCl₄) shows absorptions at 1775 (vs, C=O) and 1522 cm\(^{-1}\) (w, N=N). The visible spectrum (CCl₄) shows absorptions at 528 (\( \epsilon \) 168), 544 (\( \epsilon \) 226), 554 (\( \epsilon \) 187), and 574 nm (\( \epsilon \) 210).

**Anal.** Calcd for C₆H₅N₃O₂: C, 37.80; H, 3.97.

Found: C, 37.99; H, 4.07.

F. *p*-MethoxyphenylTAD, mp 129.5-130.0⁰ with slight decomposition, was prepared in a manner similar to that used for MeTAD in 60% yield after sublimation (0.1 mm, 60⁰). The nmr spectrum (CDCl₃) exhibits a complex multiplet at \( \tau 2.84 \) (4 H, arom.) and a singlet at \( \tau 6.18 \) (3 H, OCH₃). The infrared spectrum (CHCl₃) shows absorptions at 1765, 1732 (vs, C=O), 1602, 1584 cm\(^{-1}\) (w, C=C). The visible spectrum (CH₂Cl₂) shows absorptions at 404 (\( \epsilon \) 211) and 546 nm (\( \epsilon \) 150).

**Anal.** Calcd for C₉H₇N₃O₃: C, 52.69; H, 3.44.

Found: C, 52.71; H, 3.37.

G. *p*-NitrophenylTAD. Owing to the unstable nature of the initial residue of this compound after evaporation of solvent at reduced pressure, the preparation will be described in detail. A 100 ml round-bottom flask with 24/40 joint was charged with a slurry of 0.822 g (3.73 mmol) of
4-(p-nitrophenyl)-urazole and 10 g of anhydrous sodium sulfate in 50 ml of methylene chloride. To the slurry at room temperature a slow stream of nitrogen tetroxide was introduced until it appeared all the urazole had dissolved. After partial removal of the dinitrogen tetroxide/nitrogen dioxide in vacuo, the flask was fitted with a drying tube containing Drierite and placed in the dark. After 2 hours, the mixture was vacuum filtered to remove the sodium sulfate and the solvent removed in vacuo. Although some decomposition of the crude residue was detected, the flask containing this residue was quickly fitted with a cold finger with 24/40 joint and the apparatus was evacuated. After one sublimation (0.1 mm, 70°C), 0.190 g (0.864 mmol, 23%) of orange-red material was isolated. Another sublimation (0.1 mm, 70°C) of 0.147 g of this material afforded 0.058 g (39.2% recovery), mp 126.5-127.5°C with decomposition. The infrared spectrum (Nujol) shows absorptions at 1770 (vs, C=O), 1612 and 1598 cm⁻¹ (m, C=O). The visible spectrum (CH₂Cl₂) exhibits an absorption at 541 (ε 150) with a shoulder at 562 nm (ε 108).

Anal. Calcd for C₁₈H₁₄N₄O₄: C, 43.65; H, 1.83.

Found: C, 43.48; H, 1.76.

PhenylTAD was prepared in a manner similar to that used for MeTAD in 86% yield after two sublimations (0.1 mm,
55°). No melting point could be determined because of extensive decomposition on heating. The visible spectrum (CH₂Cl₂) shows absorption at 339 (ε 550) and 546 nm (ε 188).

I. 1,6-HexamethyleneTAD. The corresponding urazole was treated with dinitrogen tetroxide/nitrogen dioxide in the same manner as in the MeTAD preparation. However, the work-up was complicated by the low solubility of the product in methylene chloride and its resistance to sublimation. Hence the product was not fully characterized. The nmr spectrum (acetone-d₆) of the initial red residue shows a 3-lined multiplet at τ 6.39 (4 H, NCH₂) and a complex multiplet centered at τ 8.42 (8 H, CH₂).

Attempted Preparation of 1,2,4-Triazoline-3,5-dione (2). Several attempts to prepare and isolate the "parent" triazoline dione were attempted, using dinitrogen tetroxide. To slurries of urazole in dioxane, methylene chloride, diethyl ether and tetrahydrofuran at ca. -20° a slow stream of dinitrogen tetroxide was introduced. In all cases the solutions turned red, indicating the presence of triazoline dione, but when solutions were evaporated to dryness at reduced pressure the red color faded.
Reactions of 4-n-Butyl-1,2,4-triazoline-3,5-diones (2) with Various Monoolefins

A. 1-(2,3-Dimethyl-3-buten-2-yl)-4-n-buty lurazole (32).

To a red solution of 0.989 g (6.38 mmol) of n-ButAD dissolved in 50 ml of methylene chloride at 0° was added 5.06 g (60.4 mmol) of 2,3-dimethyl-2-butene. The red color was discharged within a minute. After evaporation of the solvent and excess olefin, there remained 1.45 g (6.07 mmol, 95%) of a viscous liquid which crystallized upon standing. Sublimation (0.01 mm, 45°) of 1.04 g (4.35 mmol) of the crude product afforded 1.00 g (4.18 mmol, 96% recovery) of a white solid, mp 52.0-53.5°.

The nmr spectrum (CCl₄) displays an apparent broad singlet at τ 5.12 (2 H, H₂C=C), a broad triplet at τ 6.57 (2 H, NCH₂), singlets at τ 8.22 (3 H, CH₃C=C) and 8.47 (6 H, NC(CH₃)₂), and a broad multiplet centered at τ 8.83 (7 H, CH₂CH₂CH₃). The infrared spectrum (CCl₄) shows absorptions at 1760 and 1685 cm⁻¹ (vs, C=O).

Anal. Calcd for C₁₂H₂₁N₃O₂: C, 60.23; H, 8.84.
Found: C, 60.04; H, 8.74.

B. 1-(2-Cyclohexen-1-yl)-4-n-buty lurazole (35). The adduct of n-ButAD and cyclohexene was prepared in good yield, mp 59.0-60.0°, in a manner similar to that used for adduct 32.
The nmr spectrum (CCl₄) shows multiplets centered at δ 4.20 (2 H, H₂C=CH₂), 5.31 (1 H, NCH), 6.52 (2 H, NCH₂), and δ 8.44 (13 H, CH₂CH₂CH₂ and CH₂CH₂CH₃). The infrared spectrum (CCl₄) shows absorptions at 1760 and 1686 cm⁻¹ (vs, C=O).

**Anal.** Calcd for C₁₂H₁₉N₃O₂: C, 60.74; H, 8.07.

Found: C, 60.75; H, 8.00.

**Reactions of 4-Methyl-1,2,4-triazoline-3,5-dione with Various Monoolefins**

**A. 1-(2,3-Dimethyl-3-buten-2-yl)-4-methylurazole (31).**

The adduct of MeTAD and 2,3-dimethyl-2-buten was prepared in 97% yield, mp 95.0-96.0⁰, by the same procedure described for adduct 32. The nmr spectrum (CDCl₃) exhibits an apparent broad singlet at δ 5.05 (2 H, H₂C=CH₂), and singlets at δ 6.97 (3 H, NCH₃) δ 8.19 (3 H, CH₂C=CH₂), and δ 8.42 (6 H, C(CH₃)₂). The infrared spectrum (CHCl₃) shows absorptions at 1763 and 1695 cm⁻¹ (vs, C=O).

**Anal.** Calcd for C₉H₁₅N₃O₂: C, 54.81; H, 7.67.

Found: C, 54.82; H, 7.52.

**B. 1-(2-Cyclohexen-1-yl)-4-methylurazole (33).** The adduct of MeTAD and cyclohexene was prepared in 97% yield, mp 149.0-149.5⁰, by the same procedure described for adduct 32. The nmr spectrum (CDCl₃) exhibits a multiplet at δ 4.19 (2 H, CH=CH₂), a broad multiplet at δ 5.22 (1 H, NCH), a
singlet at $\tau$ 6.92 (3 H, NCH$_3$), and a complex multiplet centered at $\tau$ 8.10 (6 H, CH$_2$CH$_2$CH$_2$). The infrared spectrum (CHCl$_3$) shows absorptions at 1760, 1659 (vs, C=O), and 1598 cm$^{-1}$ (w, C=C).


  Found: C, 55.26; H, 6.85.

C. 1-(2-Cyclopenten-1-yl)-4-methylurazol (34). The adduct of MeTAD and cyclopentene was prepared in 96% yield, mp 118.5-119.5$^\circ$, by the same procedure described for adduct 32. The nmr spectrum (CDCl$_3$) exhibits a complex multiplet at $\tau$ 4.12 (2 H, CH=CH), a broad multiplet at $\tau$ 4.72 (1 H, NCH), a singlet at $\tau$ 6.96 (3 H, NCH$_3$), and a complex multiplet centered at $\tau$ 7.88 (4 H, CH$_2$CH$_2$). The infrared spectrum (CHCl$_3$) shows absorptions at 1760, 1695 (vs, C=O), and 1615 cm$^{-1}$ (w, C=C).

Anal. Calcd for C$_8$H$_{11}$N$_3$O$_2$: C, 53.05; H, 6.12.

  Found: C, 53.24; H, 6.07.

D. 1-(3-Buten-2-yl)-4-methylurazol (30). The adduct of MeTAD and trans-2-butene was prepared by the same procedure described for adduct 32 with the exception that the gaseous trans-2-butene (Matheson Co.) was introduced without further purification into the red dione solution until the color was completely discharged. Adduct 30 was prepared in
98% yield, mp 71.0-72.0°. The nmr spectrum (CDCl₃, NMR-2) exhibits a complex multiplet centered at τ 4.33 (3 H, \( H₂C=CH\)), a broad 5-lined multiplet at τ 5.21 (1 H, NCH), a singlet at τ 6.90 (3 H, NCH₃), and a doublet at τ 8.62 (3 H, \( CCH₃\)). The infrared spectrum (CHCl₃, IR-2) shows a strong carbonyl doublet at 1760 and 1692 cm⁻¹.

**Anal.** Calcd for \( C₇H₁₁N₃O₂ \): C, 49.70; H, 6.55.
Found: C, 49.54; H, 6.45.

**E. 1-(3-Buten-2-yl)-4-methylurazole (30).** The adduct of MeTAD and cis-2-butene was prepared in 96% yield, mp 72.0-73.0°, in the same manner described for adduct 30. The nmr and infrared spectra were identical to those of the trans-2-butene adduct 30 and a mixed melting point of these two adducts is undepressed.

**Anal.** Calcd for \( C₇H₁₁N₃O₂ \): C, 49.70; H, 6.55.
Found: C, 49.85; H, 6.46.

**Qualitative Rate Comparison of the Reactions of Cyclohexene with 4-Methyl-1,2,4-triazoline-3,5-dione (2) and Diethyl Azodicarboxylate.** A 100 ml flask was charged with 0.649 g (5.74 mmol) of MeTAD dissolved in 50 ml of methylene chloride. Addition of 4.71 g (57.4 mmol) of cyclohexene to this red solution caused the color to completely disappear within 6 minutes at 25°.
In comparison, a 20 x 250 mm Pyrex combustion tube was charged with 1.00 g (5.74 mmol) of diethyl azodicarboxylate and 4.71 g (57.4 mmol) of cyclohexene dissolved in 50 ml of methylene chloride. The tube was then degassed by two freeze-pump-thaw cycles and sealed. After 6 weeks at 50 ± 1° the yellow color of the diethyl azodicarboxylate was not completely discharged.

Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione with Styrene. About 0.7 ml (0.643 g, 6.09 mmol) of styrene was added to a red solution of 0.588 g (5.20 mmol) of MeTAD dissolved in 10 ml of methylene chloride. The solution was colorless within 1 minute. The solvent was removed at reduced pressure, and the resulting residue was recrystallized from a 50:50 mixture of ethanol and water to afford 0.40 g (1.21 mmol, 46.5%) of a white crystalline 2:1 adduct, mp 280.0–280.5° with decomposition.

Anal. Calcd for C_{14}H_{14}N_{6}O_{4}: C, 50.91; H, 4.27. Found: C, 50.67; H, 4.18.

The nmr spectrum (DMSO-δ₆, NMR-3) displays a very broad resonance centered at τ -0.1 (1 H, NH), a doublet with fine structure centered at τ 1.80 (1 H, aromatic NC=CH), a complex multiplet centered at τ 2.71 (3 H, aromatic), singlets at τ 6.98 (3 H, NCH₃) and 7.09 (3 H, NCH₃), and an ABX system
with a three-lined multiplet centered at \( \tau \ 4.49 \) (1 H, NCH) and an eight-lined multiplet centered at \( \tau \ 5.98 \) (2 H, CH\(_2\)). The infrared spectrum (Nujol, IR-3) shows absorptions at 3275 (m, NH), 1777 (m, C=O), 1762 (m, C=O), 1702 (vs, C=O), 1598 (w, C=C), and 1582 cm\(^{-1}\) (w, C=C).

Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione with \( \alpha \)-Methylstyrene. A solution of 0.765 g (6.48 mmol) \( \alpha \)-methylstyrene, which had been redistilled in vacuo, in 20 ml of methylene chloride was added to a red solution of 0.609 g (5.39 mmol) MeTAD in 30 ml methylene chloride at 0\(^{\circ}\). The reaction mixture was colorless within 30 seconds. Residual \( \alpha \)-methylstyrene and solvent were removed in vacuo, affording a crude white solid which after recrystallization from ethanol yielded 0.838 g (2.43 mmol, 90\%) of a white, crystalline, solid 2:1 adduct 38, mp 232-234\(^{\circ}\) with decomposition.

**Anal.** Calcd for C\(_{15}\)H\(_{16}\)N\(_6\)O\(_4\): C, 52.31; H, 4.68.

**Found:** C, 52.35; H, 4.58.

The nmr spectrum (DMSO-d\(_6\), NMR-4) exhibits a very broad resonance centered at \( \tau \ 0.07 \) (1 H, NH), a doublet with fine structure centered at \( \tau \ 1.84 \) (1 H, aromatic NC=CH), a complex multiplet centered at \( \tau \ 2.72 \) (3 H, aromatic), singlets at \( \tau \ 7.00 \) (3 H, NCH\(_3\)), 7.18 (3 H, NCH\(_3\)), and 8.24 (3 H, CCH\(_3\)),
and an AB system at $\tau$ 5.48 and 6.28 ($2\,\text{H, } J = 13\,\text{Hz, CH}_2$).
The infrared spectrum (Nujol, IR-4) shows absorptions at
3275 (m, NH), 1762 (m, C=O), 1728 (s, C=O), 1688 (s, C=O),
1601 (w, C=C), and 1583 cm$^{-1}$ (w, C=C).

**Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione with trans-Stilbene.** A solution of 0.812 g (4.51 mmol) of trans-
stilbene in 35 ml of methylene chloride was rapidly added to
a magnetically stirred solution of 0.501 g (4.43 mmol) of
MeTAD in 25 ml of methylene chloride at 25$^\circ$. The reaction
mixture was colorless in ca. 15 minutes. The solvent was
removed at reduced pressure, and the solid residue was
triturated with hot ether to remove excess trans-stilbene.
The resulting material was recrystallized from acetonitrile,
and the isolated white solid dried overnight, in vacuo, at
50$^\circ$. After drying 0.435 g (1.07 mmol, 48%) of a 2:1 adduct,
39, mp 282.0-283.0 was isolated.

**Anal.** Calcd for C$_{20}$H$_{18}$N$_6$O$_4$: C, 59.11; H, 4.46.

**Found:** C, 59.39; H, 4.67.

The nmr spectrum (DMSO-d$_6$, NMR-5) exhibits a very broad
absorption centered at $\tau$ -0.3 (1 H, NH), a doublet with fine
structure centered at $\tau$ 1.77 (1 H, $J = 7.6\,\text{Hz, aromatic}
NC=CH$), a complex multiplet centered at $\tau$ 2.73 (8 H,
 aromatic), singlets at $\tau$ 6.92 (3 H, NCH$_3$) and 7.07 (3 H,
NCH$_3$), and an AB system with a two-lined multiplet at $\tau$ 4.08 and a two-lined multiplet at $\tau$ 4.33 (2 H, NCH=CHPh). The infrared spectrum (Nujol, IR-5) shows absorptions at 1776 (m, C=O), 1758 (m, C=O), 1727 (s, C=O), 1690 (vs, C=O), 1606 (w, C=C), and 1587 cm$^{-1}$ (w, C=C).

**Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione with 2,6-Dichlorostyrene.** To a solution of 1.13 g (10.0 mmol) of MeTAD in 25 ml of methylene chloride was added rapidly 1.73 g (10.0 mmol) of 2,6-dichlorostyrene. Moist blue litmus turned red when exposed to vapors above the reaction mixture. The red dione color was completely discharged within 2 hours. Evaporation of the solvent afforded a residue which was filtered through a column of alumina using chloroform as the eluent. The solvent was removed from the filtrate, and resulting material recrystallized from chloroform-petroleum ether (60-70$^\circ$) to afford a 0.971 g (3.4 mmol, 34%) of light yellow crystals of a 1:1 adduct 41, mp 159.5-161.0$^\circ$.

**Anal.** Calcd for C$_{11}$H$_9$Cl$_2$N$_3$O$_2$: C, 46.17; H, 3.17; Cl, 24.78.

**Found:** C, 46.23; H, 3.31; Cl, 26.08.

The nmr spectrum (CDCl$_3$, NMR-6) displays a doublet of doublets centered at $\tau$ 1.76 (1 H, aromatic NC=CH), a complex multiplet centered at $\tau$ 2.77 (3 H, aromatic), a singlet at $\tau$ 6.83 (3 H, NCH$_3$), and an ABX system with a three-lined
multiplet centered at τ 4.41 (1 H, C1CH) and an eight-lined multiplet centered at τ 5.77 (2 H, CH₂). The infrared spectrum (CHCl₃, IR-6) shows absorptions at 1776 (s, C=O), 1718 (vs, C=O), 1595 (m, C=C), and 1579 cm⁻¹ (m, C=C).

Preparation of 1-Cyclohexyl-4-n-butylurazole (42). A quartz vessel was charged with 0.415 g (2.67 mmol) of freshly sublimed n-ButTAD dissolved in 175 ml of cyclohexane, which had been purified by filtration through aluminum oxide followed by distillation under nitrogen. This solution was flushed with nitrogen for 30 minutes then irradiated under a nitrogen atmosphere in a Rayonet photochemical reactor employing 16 low-pressure mercury 2537 Å lamps at 25⁰ until the solution was colorless, approximately 1.75 hours. The solvent was removed in vacuo, and 0.563 g of a viscous liquid remained. After chromatographing this liquid on a silica gel column using diethyl ether as the eluent two major fractions were isolated. The band with the largest R_f value afforded 0.256 g of a clear liquid which was not fully characterized. The lower R_f band yielded 0.120 g (0.502 mmol, 19%) of a white solid, which following sublimation (0.01 mm, 70⁰) was obtained analytically pure, mp 72.5-73.5⁰. The nmr spectrum (CCl₄) displays an overlapping broad multiplet at τ 6.12 (1 H, NCH) and a triplet at τ 6.51 (2 H, NCH₂); and a multiplet centered
at τ 8.53 (17 H, CH₂CH₂CH₃ and (CH₂)₅). The infrared spectrum (CCl₄) shows a strong carbonyl doublet at 1757 and 1688 cm⁻¹.

**Anal.** Caled for \( \text{C}_{12}H_{21}N_{3}O_{2} \): C, 60.23; H, 8.84.

**Found:** C, 60.39; H, 8.74.

1-Cyclohexyl-4-n-butylurazole (42) was also obtained by irradiation with visible light in the following manner: A Pyrex vessel was charged with 0.406 g (2.62 mmol) of freshly sublimed n-ButTAD dissolved in 165 ml of cyclohexane. The solution was flushed with nitrogen for 30 minutes and then irradiated under a nitrogen atmosphere with a 500-W tungsten filament General Electric lamp at a distance of ca. 7 cm from the reaction vessel. A 1 cm filter solution composed of \( 2.00 \times 10^{-3} \) M \( \text{K}_{2}\text{CrO}_{4} \) and \( 6.00 \times 10^{-3} \) M \( \text{K}_{2}\text{Cr}_{2}O_{7} \) which cuts out light below 480 nm was employed, and this filter was jacketed by an ice bath. The temperature during the reaction ranged from 10 to 17 °. After 1 hour of irradiation the red solution had turned colorless. The solvent was removed in vacuo, and 0.630 g of a yellowish solid residue remained.

After sublimation a white solid, mp 71.0-72.0 ° was obtained in 92% yield. The nmr and infrared spectra were identical to those reported above.
1-Cyclohexyl-4-n-butylurazole (42) was also obtained by the hydrogenation of 1-(2-cyclohexen-1-yl)-4-n-butylurazole (35) in the following manner: a 100 ml round-bottom flask was charged with 0.485 g (2.04 mmol) of 1-(2-cyclohexen-1-yl)-4-n-butylurazole (35) dissolved in 25 ml of absolute ethanol and 0.2 g of 10% palladium on charcoal. Upon placing this magnetically stirred mixture onto a hydrogenation apparatus, the theoretical amount of hydrogen was rapidly taken up. The catalyst was removed by filtration and the solvent evaporated at reduced pressure. The resulting residue was recrystallized from ethanol and water to afford a white solid in 57% yield, mp 74.0-75.0°. The nmr and infrared spectra were identical to those reported above.

Preparation of 1-Cyclohexyl-4-methylurazole (52). A Parr hydrogenator container was charged with 6.66 g (34.1 mmol) of 1-(2-cyclohexen-1-yl)-4-methylurazole (33) dissolved in 150 ml of absolute ethanol and 2 g of 10% palladium on charcoal. The container was placed on the Parr hydrogenator and the reduction took ca. 5 minutes. The reaction mixture was filtered to remove the catalyst, and the solvent was evaporated at reduced pressure. The resulting material was recrystallized from ethanol-water to yield 5.20 g (26.4 mmol, 77%) of white needlelike crystals, mp 138.0-139.0°. The
nmr spectrum (CDCl$_3$) exhibits a broad resonance at $\tau$ 9.33 (1H, NH), a broad multiplet at $\tau$ 6.73 (3 H, NCH$_3$) and a complex multiplet centered at $\tau$ 8.41 (10 H, (CH$_2$)$_5$). The infrared spectrum (CH$_2$Cl$_2$) shows a strong carbonyl doublet at 1760 and 1695 cm$^{-1}$.


**Photolysis of 4-Methyl-1,2,4-triazoline-3,5-diones (2) in 1,4-Dioxane.** A quartz vessel was charged with 1.831 g (16.2 mmol) of MeTAD dissolved in 73 ml of 1,4-dioxane, which was purified by distillation from lithium aluminum hydride. The vessel was sealed with a rubber serum cap and flushed for 30 minutes at 25$^\circ$ in the dark. The solution was then irradiated under a nitrogen atmosphere in a Rayonet photochemical reactor using 16 mercury vapor 2537 Å lamps at 27 $\pm$ 3$^\circ$. After 6 hours the initial red color was completely discharged.

After evaporation of the solvent at reduced pressure, a crude material was isolated and sublimed (0.01 mm, 120$^\circ$) to yield (63.4%) an analytically pure white solid adduct 43, mp 174.0-175.0$^\circ$. The nmr spectrum (CF$_3$COOH, NMR-7) displays a triplet at $\tau$ 4.26 (1 H, NCH), a complex multiplet centered at $\tau$ 5.79 (6 H, CH$_2$OCH$_2$CH$_2$), and a singlet at $\tau$ 6.71 (3 H, NCH$_3$). The infrared spectrum (Nujol, IR-7) shows a strong carbonyl doublet at 1786 and 1705 cm$^{-1}$. 
Anal. Calcd for $C_{7}H_{11}N_{3}O_{4}$: C, 41.79; H, 5.51.
Found: C, 41.77; H, 5.40.

Reaction of Several 4-Substituted-1,2,4-triazoline-3,5-diones (2) with Cumene

A. p-MethoxyphenylTAD. A 25 x 200 mm Pyrex test tube was charged with 0.337 g (1.65 mmol) of freshly sublimed p-methoxyphenylTAD dissolved in 50 ml of cumene which was purified by two washings with conc. $H_{2}SO_{4}$, then filtration through a column of alumina, followed by a vacuum distillation (3.0 mm, 27°C). The test tube was sealed with a serum cap and flushed with nitrogen at 25°C in the dark for 30 minutes. The solution was then irradiated to colorlessness with 500 W General Electric projector lamp, which was cooled by a water jacket and a stream of nitrogen. The temperature during irradiation was 23 ± 1°C. The solvent was removed at reduced pressure and 0.492 g (1.51 mmol, 92%) of crude 1-cumyl-4-(p-methoxyphenyl)-urazole (42) was isolated. This material was twice recrystallized from acetone, then sublimed (0.01 mm, 155°C) to afford an analytically pure white solid, mp 166.0-167.0°C. The nmr spectrum (DMSO-d$_6$) exhibits overlapping multiplets at $\tau$ 2.90 (9 H, aromatic), and singlets at $\tau$ 6.28 (3 H, OCH$_3$) and $\tau$ 8.24 (6 H, NC(CH$_3$)$_2$). The infrared spectrum (Nujol) shows a strong carbonyl doublet at 1763 and 1686 cm$^{-1}$. 
Anal. Calcd for C_{18}H_{19}N_{3}O_{3}: C, 66.45; H, 5.89.
     Found: C, 66.09; H, 6.02.

B. PhenylTAD. 1-Cumyl-4-phenylurazole (46), mp 153.0-
               153.5°, was prepared in a manner similar to that described
               above. The nmr spectrum (CDCl₃) shows a multiplet centered
               at τ 2.66 (10 H, aromatic) and a singlet at τ 8.23 (6 H,
               NC(CH₃)₂). The infrared spectrum (Nujol) exhibits a
               strong carbonyl doublet at 1768 and 1692 cm⁻¹.

Anal. Calcd for C_{17}H_{17}N_{3}O_{2}: C, 69.14; H, 5.80.
     Found: C, 68.85; H, 5.78.

C. MethylTAD. 1-Cumyl-4-methylurazole (44), mp 126.5-
               127.0°, was prepared in a manner similar to that described
               above. The nmr spectrum (DMSO-d₆) shows a multiplet at τ
               2.68 (5 H, aromatic) and singlets at τ 7.15 (3 H, NCH₃)
               and τ 8.29 (6 H, NC(CH₃)₂). The infrared spectrum (Nujol)
               exhibits a strong carbonyl doublet at 1753 and 1680 cm⁻¹.

Anal. Calcd for C_{12}H_{15}N_{3}O_{2}: C, 61.79; H, 6.48.
     Found: C, 61.51; H, 6.43.

1-Cumyl-4-methylurazole (44) was also prepared by
allowing MeTAD to react with cumene in the dark. A 25 x 200
mm Pyrex test tube was charged with 1.02 g (9.02 mmol) of
MeTAD dissolved in 50 ml of cumene. The test tube was
sealed with a serum cap and placed in the dark at room
temperature. After the color was completely discharged, the solvent was removed at reduced pressure. The resulting white residue was recrystallized from ethanol-water to yield 0.769 g (3.30 mmol, 37%) of white crystals, mp 126.5-127.5\(^\circ\). The nmr and infrared spectra are identical to those of the photoproduct.

**Kinetics of Photochemical Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione (2) with Cumene.** A Pyrex cell containing a solution of MeTAD in cumene was degassed by three freeze-pump-thaw cycles and then sealed under vacuum. The visible spectrum of this solution shows an absorption maximum at 538.5 nm with an absorbance of 1.78. We had previously determined the extinction coefficient of MeTAD in cumene to be 256 at 538.5 nm; therefore, the concentration of this solution is 6.95 x 10\(^{-3}\) M. This solution was then irradiated using a 500-W General Electric tungsten lamp cooled with air and a water condenser. The Pyrex cell was cooled with water, and the temperature of the water was maintained at ca. 17\(^\circ\). Periodically during irradiation, the absorption at 538.5 nm was measured for several minutes to follow the reappearance of MeTAD. After ca. 10.5 minutes, the change in absorption was considered minimal, and this value was subtracted from the absorption of MeTAD prior to the irradiation interval. The resulting value was used to calculate the MeTAD concen-
tration which had disappeared. The slope of a plot of the logarithm of this calculated value of the MeTAD concentration as a function of time irradiated gives a pseudo-first-order rate constant, \( k = 4.30 \times 10^{-2} \text{ min}^{-1} \), for the disappearance of MeTAD.

**General Procedure for Examination of Extent of Monomer Regeneration of 4-Alkyl-1,2,4-triazoline-3,5-dione Photopolymers.** Solutions \( 10^{-2} \) to \( 10^{-3} \) M of different triazoline diones in various solvents were prepared. The solutions were placed in 1 cm\(^2\) Pyrex glass cells and sometimes were degassed by several freeze-pump-thaw cycles and then sealed. The visible absorption spectra of these solutions were measured on the Cary 14 prior to irradiation. The solutions were then irradiated in the Pyrex cells using a Sawyer Rotomatic slide projector with a General Electric 500-W tungsten lamp as a visible light source. After irradiation the visible absorption spectra were measured to determine extent of disappearance of triazoline dione if the solution was not completely colorless, and further visible absorption spectra were taken to measure extent of regeneration with time.

**Osmometric Molecular Weight Determinations of 4-n-Butyl-1,2,4-triazoline-3,5-dione Photopolymer.** A 0.3 M solution of n-BuTAD (twice sublimed) in carbon tetrachloride (spec. grade,
Mallinckrodt, filtered through a column of alumina) was irradiated until colorless (8 minutes at ca. 21 ± 1⁰) using a 150 W quartz-iodine tungsten lamp. The solution was purged with a continuous stream of nitrogen 5 minutes prior to and during the irradiation. Measurements were made on the regenerating solution using a Mechrolab Vapor Pressure Osmometer, Model 301A, thermostated at 25 ± 0.2⁰. Approximately 4 minutes after irradiation, the first measurement from the osmometer indicated an apparent molecular weight of 4200. After 30 minutes the molecular weight dropped to 2700 and ca. 4% (estimated from visible spectrum) of the red monomer had regenerated. With the exception that usually the vapor pressure osmometer was thermostated at 37 ± 0.2⁰, this was the general procedure for obtaining molecular weight data for the photopolymers.

Lyophilization of 4-n-Butyl-1,2,4-triazoline-3,5-dione

Photopolymer in Carbon Tetrachloride. About 3.0 ml of a 0.60 M solution of n-ButAD in carbon tetrachloride was irradiated until colorless within 16 minutes at ca. 21⁰ using a 150 W quartz-iodine tungsten lamp with a continuous stream of nitrogen bubbling through the solution 10 minutes prior to and during irradiation. The photobleached solution was quickly transferred to a 250 ml round-bottom flask
which was attached to a Dewar condenser. The flask was rotated in a liquid nitrogen bath to produce a thin solid film of material. Liquid nitrogen was placed in the condenser and a vacuum \((0.1-0.2 \text{ mm})\) applied. After about 10 minutes the liquid nitrogen in condenser and bath was changed to Dry Ice/iso-propyl alcohol. This material was lyophilized for a total of 18 hours to afford a faintly pink glass.

**Anal.** Calcd for monomer unit \(\text{C}_6\text{H}_9\text{N}_3\text{O}_2\):

\[
\begin{aligned}
\text{C}, & \text{ 46.45; H, 5.85; Cl, 0.00.} \\
\text{Found:} & \\
\text{C}, & \text{ 46.10; H, 5.61; Cl, 1.44.}
\end{aligned}
\]

Reaction of 1-Cyclohexyl-4-methylurazole (52) with Diazomethane. To a solution of 0.805 g (4.08 mmol) of 1-cyclohexyl-4-methylurazole (52) in \(\text{ca. 20 ml methylene chloride}\) a yellow solution of freshly distilled diazomethane in ether \(\text{62}\) was added dropwise until the solution no longer decolorized the diazomethane solution. The solvent and excess reagent were removed \text{in vacuo} and 0.890 g of a clear viscous oil remained. The nmr spectrum \((\text{CCl}_4)\) of this oil exhibits a broad multiplet at \(\tau 8.43\) and four singlet peaks at \(\tau 6.99, 6.88, 6.83\) and 6.01, indicating the presence of both the 0-methylated and N-methylated isomers in a 1:3 ratio. Approximately 400 mg of this oil was chromatographed on a column of
0.05-0.2 mm silica gel (Brinkmann) using ether as the eluent. Upon evaporation of ether from the fraction with the higher Rf value, 262 mg of a clear viscous oil remained. This oil was purified by molecular distillation (0.2 mm, 55°). The purified oil was identified as 1-cyclohexyl-2,4-dimethylurazole (54).

**Anal.** Calcd for C10H17N3O2: C, 56.85; H, 8.11.

Found: C, 56.53; H, 8.17.

The nmr spectrum (CCl4, NMR-8) displays a very broad multiplet at τ 6.46 (1 H, NCH), two singlets at τ 6.91 (3 H, NCH3) and τ 7.04 (3 H, NCH3), and a broad multiplet at τ 8.43 (10 H, C5H10). The infrared spectrum (CCl4, IR-8) displays a carbonyl doublet at 1760 cm⁻¹ and 1705 cm⁻¹.

Evaporation of solvent from the lower Rf component yielded 95 mg of a pale yellow solid. Sublimation (0.2 mm, 55°) resulted in a white solid, mp 97.0-98.0, identified as 1-cyclohexyl-3-methoxy-4-methylurazole (53).

**Anal.** Calcd for C10H17N3O2: C, 56.85; H, 8.11.

Found: C, 57.12; H, 8.04.

The nmr spectrum (CCl4, NMR-9) shows a singlet at τ 6.09 with an overlapping broad multiplet (4 H, NCH and OCH3), a singlet at τ 6.97 (3 H, NCH3), and a broad multiplet at τ 8.43 (10 H, C5H10). The infrared spectrum (CCl4, IR-9)
shows a carbonyl singlet at 1705 cm\(^{-1}\) and two intense peaks at 1605 cm\(^{-1}\) and 1513 cm\(^{-1}\) attributed to the imidate-like functionality.

**Infrared Examination of Carbonyl Intensity of 4-n-Butyl-1,2,4-triazoline-3,5-dione Photopolymer and Model Compounds.** A 0.03 M solution of n-BuTAD in carbon tetrachloride flushed 5 minutes with nitrogen was irradiated to a colorless state in 26 minutes using a 150 W quartz-iodine tungsten lamp. Using a Perkin Elmer Model 521 spectrophotometer the absorption spectra between 1900 and 1600 cm\(^{-1}\) were recorded for the following 0.03 M carbon tetrachloride solutions: n-BuTAD, n-BuTAD photopolymer, 1-cyclohexyl-4-methylurazole (52), 1-cyclohexyl-2,4-dimethylurazole (54), and 1-cyclohexyl-3-methoxy-4-methylurazole (53). The carbonyl bands in this area were then plotted with absorbance vs frequency (cm\(^{-1}\)). Xeroxed copies of these graphs were made, and the areas cut out and weighed. The resulting relative areas of the carbonyl bands of the compounds above are as follows: 1.51:1.80:2.20:2.00:1.01.

**Preparation of 4-n-Butyl-1,2,4-triazoline-3,5-dione Photopolymer.** A 0.3 M solution of n-BuTAD (twice sublimed) in carbon tetrachloride (spec. grade, Mallinckrodt, filtered through a column of alumina) was irradiated until colorless
(8 minutes at ca. 21 ± 1°) using a 150-W quartz-iodine tungsten lamp. The solution was purged with a continuous stream of nitrogen 5 minutes prior to and during the irradiation.

The 220 MHz nmr spectrum (CCl₄, NMR-10) exhibits a very broad resonance centered at τ 2.65 (NH) and four broad featureless bands at τ 5.34, 8.29, 8.54, and 8.98 (NCH₂CH₂CH₂CH₃). The infrared spectrum (CCl₄, IR-10) shows absorptions at 3220 (w, NH), 1814 (m, C=O), and 1750 cm⁻¹ (vs, C=O).

Effect of Pyridine on the Regeneration of 4-n-Butyl-1,2,4-triazoline-3,5-dione Photopolymer. A 0.3 M stock solution of n-BuTAD in carbon tetrachloride was prepared. One milliliter of this solution was volumetrically diluted to 50 ml with carbon tetrachloride, and a visible spectrum of the resulting solution shows an absorbance maximum of 1.39 at 545 nm (ε 232). Approximately 4 ml of the 0.3 M stock solution flushed 5 minutes with nitrogen were irradiated to colorlessness in 8 minutes at ca. 21 ± 1° using a 150-W quartz-iodine tungsten lamp. One milliliter of the photobleached solution was volumetrically diluted to 50 ml with carbon tetrachloride, and ca. 10 drops of pyridine were added. After about 30 minutes a visible spectrum showed an absorbance of 0.97 at 545 nm indicating 70% regeneration of red monomer. In comparison, 1 ml of photobleached solution diluted volumetrically
to 50 ml with carbon tetrachloride and not treated with pyridine has a visible spectrum which showed an absorbance of 0.15 at 545 nm indicating 11% regeneration of red monomer after 30 minutes. Another 1 ml portion of the photobleached solution was treated with several drops of a solution of diazomethane in diethyl ether until a yellow color persisted. Solvent and excess reagent were removed in vacuo, the residue volumetrically diluted to 50 ml with carbon tetrachloride, and ca. 10 drops of pyridine added. Approximately 15 minutes later a visible spectrum shows an absorbance of 0.07 at 545 nm indicating 5% regeneration of red monomer.

Reaction of 4-n-Butyl-1,2,4-triazoline-3,5-dione Photopolymer with Diazomethane. A solution of 3-4 ml of 0.3 M n-ButTAD flushed 5 min with nitrogen was irradiated to colorlessness in 8 min using a 150-W quartz-iodine tungsten lamp. To a portion of this colorless solution, a freshly prepared solution of diazomethane in ether was added until a faint yellow color persisted. Solvent and excess reagent were evaporated in vacuo. Carbon tetrachloride was added to the residue and to a portion of the resulting solution a few drops of pyridine were introduced with no dramatic change in color observed. A 220 MHz nmr spectrum (CCl₄, NMR-11) of the pyridine-free portion displays four broad peaks at
\( \tau 6.34, 8.29, 8.34 \) and 8.98 attributable to the four types of protons in the \( n \)-butyl groups. In addition, two smaller broad peaks of similar intensity at \( \tau 6.08 \) and 6.93 may be assigned to terminal 0-methylated and \( N \)-methylated groups. The infrared spectrum (CCl\(_4\), IR-11) displays an intense carbonyl band centered at 1740 cm\(^{-1}\) with a shoulder at 1812 cm\(^{-1}\) and two broad weak bands at 1610 and 1495 cm\(^{-1}\) associated with the 0-methylated end groups.

**Effect of Diazomethane on the Regeneration of 4-\( n \)-Butyl-1,2,4-triazoline-3,5-dione Photopolymer.** A 0.3 M stock solution of \( n \)-Butyl Azo in carbon tetrachloride was prepared. One milliliter of this solution was volumetrically diluted to 50 ml with carbon tetrachloride, and a visible spectrum of the resulting solution showed an absorbance maximum of 1.39 at 545 nm (\( \epsilon 232 \)). Approximately 4 ml of the 0.3 M stock solution flushed with nitrogen for 5 minutes were irradiated to colorless in 8 minutes at \( \epsilon 21 \pm 1^0 \) using a 150-W quartz-iodine tungsten lamp. One milliliter of the photobleached solution was volumetrically diluted to 50 ml with carbon tetrachloride. Another 1 ml portion of the photobleached solution was treated with several drops of a solution of diazomethane in diethyl ether until a yellow color persisted. Solvent and excess reagent were removed in vacuo, and the
residue volumetrically diluted to 50 ml with carbon tetrachloride. The regeneration of red monomer was monitored by visible spectroscopy.

**Reaction of 4-\textit{\textbeta}-Butyl-1,2,4-triazoline-3,5-dione with Diazomethane.** To a solution of 1.07 g (6.39 mmol) of \textit{\textbeta}-BuTAD in methylene chloride was added a freshly distilled solution of diazomethane in ether until the red dione color disappeared. After solvent was removed by vacuum and the residue dried for 24 hrs, 1.189 g of a white glassy solid resulted. An osmometric molecular weight determination using a concentration of 55 mg/ml of carbon tetrachloride indicated a polymer of number average molecular weight 3390. A 220 MHz nmr spectrum (CCl₄, NMR-12) shows four intense featureless bands at τ 9.02, 8.71, 8.43 and 6.44 associated with protons of \textit{\textbeta}-butyl groups; a broad band centered at τ 4.20 (NCH₂N or OCH₂N); and two less intense bands at τ 7.00 and 6.08 attributed to O-methylated and N-methylated end groups, respectively. The infrared spectrum (CCl₄, IR-12) displays an intense carbonyl doublet at 1775 and 1712 cm⁻¹ and less intense bands at 1601 and 1495 cm⁻¹ associated with imidate-like functionality.

**Attempt to Initiate Polymerization of 4-\textit{\textbeta}-Butyl-1,2,4-triazoline-3,5-dione (2) with 2,2'-Azobis-(2-methylpropio-**
nitrile). To a 3.0 M solution of \( \text{n-BuTAD} \) in carbon tetrachloride a few milligrams of 2,2'-azobis-(2-methylpropionitrile) were added. The solution was heated near boiling for several minutes, and after standing for ca. 1 hour no decoloration was observed by visual inspection.

**Effect of Solvent on Regeneration of 4-\( \text{n} \)-Butyl-1,2,4-triazoline-3,5-dione Photopolymer.** A few milliliters of 0.3 M solution of \( \text{n-BuTAD} \) in carbon tetrachloride flushed 5 min with nitrogen were irradiated to colorless in 7 min using a 150-W quartz-iodine tungsten lamp. The solvent was removed *in vacuo* from a 1 ml portion of the photobleached solution; the residue was then volumetrically diluted to 50 ml with methylene chloride. After ca. 1 day, a visible spectrum of this solution shows an absorbance maximum of 0.86 at 536 nm indicating 69% regeneration of red monomer.

In comparison, a solution of the same concentration of 4-\( \text{n} \)-BuTAD photopolymer in carbon tetrachloride has a visible spectrum after ca. 1 day which shows an absorbance maximum of 0.46 at 545 nm indicating 37% regeneration of red monomer.

**Effect of Oxygen Upon Photolysis of 4-\( \text{n} \)-Butyl-1,2,4-triazoline-3,5-dione (2) in Carbon Tetrachloride.** Two milliliters of a 0.10 M solution of \( \text{n-BuTAD} \) in carbon tetrachloride were irradiated until colorless within 6 min
at about 21° using a 150-W quartz-iodine tungsten lamp with a continuous stream of nitrogen through the solution 5 min prior to and during irradiation. In comparison, 2 ml of a similar solution required ca. 45 minutes of irradiation to attain a colorless state in the absence of a nitrogen flush.
SUMMARY

This study was undertaken to examine several thermal and photochemical modes of reaction of the highly reactive species, 4-substituted-1,2,4-triazoline-3,5-dione (2). Several of the diones with 4 substituents (methyl, ethyl, n-butyl, t-butyl, cyclohexyl, phenyl, p-methoxyphenyl, and p-nitrophenyl) were prepared in the course of this research by the oxidation of the corresponding 4-substituted urazole (1) by dinitrogen tetroxide/nitrogen dioxide.

In this study the 1:1 adducts of 4-n-butyl-1,2,4-triazoline-3,5-dione with cyclohexene and 2,3-dimethyl-2-butene and the 1:1 adducts of 4-methyl-1,2,4-triazoline-3,5-dione with cyclohexene, cyclopentene, 2,3-dimethyl-2-butene, trans-2-butene, and cis-2-butene were prepared in quantitative yields by the simple addition of the olefin to a methylene chloride solution of the triazoline dione. The structure of the adducts arising from the addition with aliphatic olefins indicates that a shift in the position of the double bond has occurred.

The reactions of 4-methyl-1,2,4-triazoline-3,5-dione with styrene, o-methylstyrene, and trans-stilbene resulted
in the formation of 2:1 adducts, 12-methyl-3-(4-methylurazol-1-yl)-1,10,12-triazatricyclo[8.3.0.0^4,9]trideca-4,6,8-triene-11,13-dione (37), 3,12-dimethyl-3-(4-methylurazol-1-yl)-1,10,12-triazatricyclo[8.3.0.0^4,9]trideca-4,6,8-triene-11,13-dione (38), and 12-methyl-2-phenyl-3-(4-methylurazol-1-yl)-1,10,12-triazatricyclo[8.3.0.0^4,9]trideca-4,6,8-triene-11,13-dione (39). These bis-adducts presumably arise from an initial Diels-Alder addition of dione to substrate followed by an additive-substitution type reaction analogous to the reaction of diones with monoolefins. However, the reaction of MeTAD with 2,6-dichlorostyrene afforded the 1:1 adduct, 3,5-dichloro-12-methyl-3-(4-methylurazol-1-yl)-1,10,12-triazatricyclo[8.3.0.0^4,9]trideca-4,6,8-triene-11,13-dione (41).

Several triazoline diones underwent photoreactions with hydrogen-donating substrates such as cyclohexane, cumene, and 1,4-dioxane to yield 1:1 addition products. However, when 4-\text{\textit{n}}-butyl-1,2,4-triazoline-3,5-dione was irradiated in such solvents as carbon tetrachloride a nitrogen-backboned polymer resulted which was unstable in solution and regenerated the bulk (60-80%) of the monomer after several days. The polymer appeared to be terminated with hydrogens and depolymerization was catalyzed by the mild base, pyridine.
thermal stability of the polymer was greatly enhanced when the polymer was treated with diazomethane to cap the ends with methyl groups.
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APPENDIX

Nuclear Magnetic Resonance Spectra

This section contains nmr spectra of several compounds described in the Results and Discussion section and Experimental section. The name of the compound, the solvent in which the compound was dissolved, and other pertinent information is given on the page facing the corresponding spectrum.
NMR-1. 4-n-Butyl-1,2,4-triazoline-3,5-dione (2, R = n-Bu) in CC\textsubscript{4} (220 MHz, 2500 Hz).

NMR-2. 1-(3-Buten-2-yl)-4-methylurazole (30) in CDCl\textsubscript{3} (50 MHz, 500 Hz). Signal at \(\tau\ 2.56\) is chloroform absorption.

NMR-3. 12-Methyl-3-(4-methylurazol-1-yl)-1,10,12-triazatri-cyclo[8.3.0.0\textsuperscript{4,9}]trideca-4,6,8-triene-11,13-dione (37) in DMSO-d\textsubscript{6} (60 MHz, 500 Hz). Multiplet at \(\tau\ 7.52\) is solvent absorption.

NMR-4. 3,12-Dimethyl-3-(4-methylurazol-1-yl)-1,10,12-triazatri-cyclo[8.3.0.0\textsuperscript{4,9}]trideca-4,6,8-triene-11,13-dione (38) in DMSO-d\textsubscript{6} (60 MHz, 500 Hz). Multiplet at \(\tau\ 7.51\) is solvent absorption.
NMR-5. 12-Methyl-2-phenyl-3-(4-methylurazol-1-yl)-1,10,12-triazatricyclo[8.3.0.0^4,9]trideca-4,6,8-triene-11,13-dione (32) in DMSO-d$_6$ (60 MHz, 500 Hz). Multiplet at $\tau$ 7.50 is solvent absorption.

NMR-6. 3,5-Dichloro-12-methyl-1,10,12-triazatricyclo[8.3.0.0^4,9]trideca-4,6,8-triene-11,13-dione (41) in CDCl$_3$ (60 MHz, 500 Hz).

NMR-7. 1-(1,4-Dioxan-2-yl)-4-methylurazole (43) in trifluoroacetic acid (60 MHz, 500 Hz).

NMR-8. 1-Cyclohexyl-2,4-dimethylurazole (54) in CCl$_4$ (60 MHz, 500 Hz).
NMR-9. 1-Cyclohexyl-3-methoxy-4-methylurazole (53) in CCl₄ (60 MHz, 500 Hz).

NMR-10. Photopolymer from irradiation of 4-\textit{n}-butyl-1,2,4-triazoline-3,5-dione in CCl₄ (220 MHz, 2500 Hz).

NMR-11. Diazomethane treated photopolymer from irradiation of 4-\textit{n}-butyl-1,2,4-triazoline-3,5-dione in CCl₄ (220 MHz, 2500 Hz).

NMR-12. Copolymer of 4-\textit{n}-butyl-1,2,4-triazoline-3,5-dione with diazomethane in CCl₄ (220 MHz, 2500 Hz).
Infrared Spectra

This section contains infrared spectra of several compounds described in the Results and Discussion section and Experimental section. The name of the compound, the solvent in which the compound was dissolved, and other pertinent information is given on the page facing the corresponding spectrum.
IR-1. 4-n-Butyl-1,2,4-triazoline-3,5-dione (2, R = n-Bu) (CCl₄).

IR-2. 1-(3-Buten-2-yl)-4-methylurazole (30) (CHCl₃).

IR-3. 12-Methyl-3-(4-methylurazol-1-yl)-1,10,12-triazatricyclo[8.3.0.0⁴,⁹]trideca-4,6,8-triene-11,13-dione (37) (Nujol).

IR-4. 3,12-Dimethyl-3-(4-methylurazol-1-yl)-1,10,12-triazatricyclo[8.3.0.0⁴,⁹]trideca-4,6,8-triene-11,13-dione (38) (Nujol).
IR-5. 12-Methyl-2-phenyl-3-(4-methylurazol-1-yl)-1,10,12-triazatricyclo[8.3.0.0^4,9]trideca-4,6,8-triene-11,12-dione (39) (Nujol).

IR-6. 3,5-Dichloro-12-methyl-1,10,12-triazatricyclo[8.3.0.0^4,9]trideca-4,6,8-triene-11,13-dione (41) (CHCl₃).

IR-7. 1-(1,4-Dioxan-2-yl)-4-methylurazole (43) (Nujol).

IR-8. 1-Cyclohexyl-2,4-dimethylurazole (54) (CCl₄).
IR- 9. 1-Cyclohexyl-3-methoxy-4-methylurazole (53) (CCl₄).

IR-10. Photopolymer from irradiation of 4-ι-butyl-1,2,4-triazoline-3,5-dione (CCl₄).

IR-11. Diazomethane treated photopolymer from irradiation of 4-ι-butyl-1,2,4-triazoline-3,5-dione (CCl₄).

IR-12. Copolymer of 4-ι-butyl-1,2,4-triazoline-3,5-dione with diazomethane (CCl₄).
VITA

Joseph Collier Stickler was born on February 19, 1942, in Piqua, Ohio where he attended Spring Street Elementary School. He was graduated from Fairlawn High School near Sidney, Ohio in 1960. He became a student of chemistry at Ohio Wesleyan University in Delaware, Ohio, receiving a Bachelor of Arts Degree with Honors in June, 1964.

He entered Graduate College at the University of Illinois at Champaign-Urbana in September, 1964, as a graduate student in organic chemistry. From September, 1964 until January of 1970 he was a half-time teaching assistant in the Department of Chemistry, University of Illinois. From September, 1965 until June, 1968 he was designated as a premium teaching assistant. In the summer of 1966 he was a research assistant through funds supplied by the Rohm and Haas Co. Again in the summer of 1967 he was a research assistant through funds supplied by the Research Corporation Decarboxylation, and during the summers of 1968 and 1967 he was a research assistant through funds supplied by the E. I. du Pont de Nemours Corporation. He received his Master of Science Degree from the University of Illinois in June, 1967.
He is a member of the American Chemical Society and Phi Beta Kappa. He is the co-author of three publications which pertain to his doctoral research. The first, "An Improved Synthesis of 1,2,4-Triazoline-3,5-diones" appeared in the Journal of Organic Chemistry in 1966; the second, "The Reaction of 1,2,4-Triazoline-3,5-diones with Mono-olefins" appeared in Chemical Communications in 1967; and the third, "Nitrogen-Backboned Polymers. I" appeared in the Journal of the American Chemical Society in 1970.