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**INTRODUCTION**

Peroxides of the types $\mathbf{2}$ or $\mathbf{3}$ (fig. 1) are of interest to Prof. G. B. Schuster for use in chmiluminescent studies. J.-y Koo proposed the mechanistic pathway for the formation of the peroxide $\mathbf{2}$ or $\mathbf{3}$ from the ozonolysis of $\mathbf{1}$. (refer to fig.1) In support of Koo's mechanism, Schuster and Hurst (in press) ozonated diphenylvinylene carbonate $\mathbf{a}$ and isolated the analogous peroxide to $\mathbf{3}$ (see fig. 2), the dibenzoylmethanoperoxycarbonate $\mathbf{b}$. Based on this rationale and precedent, the following work was aimed at the synthesis of compound $\mathbf{1}$. 
Figure 1

1. \[ \text{reaction} \] \[ \overset{\text{m/e} 70}{\longrightarrow} \]

2. \[ \text{products} \]

3. \[ \text{structure} \]

Figure 2:

[structural formula]

\[ \text{reaction} \] \[ O_3 \] \[ \text{products} \]

\[ \text{Ph - C - O - O - C - Ph} \]
DISCUSSION AND RESULTS

Two schemes have been pursued in the synthesis of 1, unfortunately, both alternatives present synthetic difficulties. Figure 3, shows the overall synthetic routes attempted while the difficulties are as follows.

Scheme 1 (Fig. 3) presents no unmanageable problem in the initial three steps. However, problems arise in the dehalogenation of 6. Four dehalogenating reagents were used in widely varied reaction conditions with limited success, each of these will be discussed here. Three of these reagents were heterogeneous metal catalyst, and the fourth, a metal complex.

1) Zinc metal either alone or in the presence of acetic acid proved to be too harsh a reagent and only anthracene was recovered.

2) Zinc-copper couple gave one successful yield of 1 (J.-Y. Koo's work), however, the problem here is control. After making several batches of this couple it was noted that reaction times for dechlorination of 6 ranged from 2 hrs. to 17 hrs. In every attempt to dehalogenate 6 using zinc-copper couple only trace amounts of 1 were observed and not isolated.

3) Starting with a large excess of magnesium metal adding iodine initially and during the reaction sequence, proved to be the most promising reagent. By adding the iodine during the experiment the activity did seem to be under more control,
however, the addition and timing is extremely critical and the result is a mixture of anthracene, \( \text{I} \), \( \text{6} \), and the hydrolysis decomposition product. The RF values of these compounds range from 0.41 to 0.69 in 10% hexane/90% methylene chloride on silica gel, so the separation is quite difficult. An isolated experiment did yield 15% (62mg) \( \text{I} \).\(^8\)

4) Bis(trimethylisilyl)mercury\(^9-12\) has many advantages:
   a) It is a homogeneous reagent.
   b) Unlike the first three reagents, bis(trimethylisilyl) mercury is stereospecifically cis, suggesting a one stage molecular mechanism for the 1,2-elimination.\(^13\)
   c) It decomposes upon reaction to inert by-products posing no threat to resulting \( \text{I} \) in the reaction. Unfortunately, it is not powerful enough to remove the chlorines from \( \text{6} \). After refluxing bis(trimethylisilyl)mercury in tetrahydrofuran for 3 hours, only \( \text{6} \) was present with some trace of unknown by-products.

Based upon the lack of success in dechlorinating \( \text{6} \) and noting the success of examples in the literature for deamination, as opposed to dechlorination, due to C-Br bonds being weaker than C-Cl bonds, hence, bromine's better leaving ability, scheme II (fig.3) was devised. As mentioned before, synthetic difficulties are again present. The first three steps successfully yielded compound \( \text{9} \).\(^{14-16}\) (noting the suggestions present in the experimental section) The dehydrohalogenation of \( \text{9} \) to yield \( \text{I} \)\(^17\) was not successful and due to time limitations had to
be dropped. It should be mentioned that triethylamine was used in the literature \(^{17}\) preparations of 10. Preliminary results show that 1,8-diazabicyclo[5.4.0]undec-7-one (DBU) \(^{18}\) gave superior conversion to 10 in situ, however, due to the instability of 10, polymerization during distillation repeatedly denied the purification of 10 in necessary quantities.
Scheme I

Scheme II
CONCLUSION

Scheme I is attractive since we lose only one step from 1, however, this fact can be deceiving since more harsh reaction conditions are required to dechlorinate than debrminate. These conditions result in a low yield reaction that requires chromatography on an easily hydrolysed compound. Attempts to scale up this dechlorination have failed. Scheme II, on the other hand, would make the necessary reaction conditions more mild if compounds 13 or 14 were made. This would probably result in higher yields of 1 and the chromatography could possibly be replaced by simple recrystallization. Speculating one step further, if a known debrminating reagent such as bis(trimethylsilyl)mercury\textsuperscript{9-12} were used, extremely mild reaction conditions could be employed resulting in inert and easily separable by-products. The disadvantages of scheme II as discussed previously in the dehalohydrogenation steps are also complicated by the question of success in the Diels-Alder reaction in converting 12 to 13 and 10 to 14.\textsuperscript{14} However, examples of all the required steps to obtain 13 and 14 are present in the literature. 14-16,19

In conclusion, I feel efforts in obtaining 1 shall continue to follow both scheme I and scheme II concurrently.
EXPERIMENTAL

Tetrachloroethylene Carbonate (4) A solution of 25g of ethylene carbonate was placed in a photochemical immersion reactor in 275 ml of carbon tetrachloride. A 450 watt Hanovia mercury vapor lamp equipped with a pyrex filter was used. The solution was stirred and chlorine gas was slowly bubbled through the reaction mixture for 24 hours. The reaction was followed by g.l.c. and n.m.r. and resulted in 53.4g of 4 (83.2% yield).

Dichlorovinylene Carbonate (5) To a solution of 10g of 4 in 50ml dry ether was added 4 drops of N,N-dimethylformamide and 8g of zinc-copper couple. The reaction mixture was stirred at 50°C for 6 hours. After removing the ether the resulting liquid was distilled at 4.5mm Hg at 24°-28°C using a micro-distillation apparatus. This gave 3.48g of 5 (51% yield). It should be noted that the distillation step here could be avoided and the resulting liquid could simply be reacted directly with anthracene, since significant amounts of 5 is lost to polymerization during the distillation step.

Dichloro Diels-Alder Adduct (6) A mixture of 4.45g distilled 5 with 3.57g anthracene was stirred and refluxed for 8 days in 50ml xylene. (reaction followed by tlc and gic) Upon cooling the reaction mixture a precipitate formed. The solid was collected and chromatographed using silica gel with 50/50 ethylene chloride-hexane. The n.m.r. of chromatographed material showed 99% pure 6 with anthracene as the balance. The
reaction gave 4.4g (58% yield) of 6. It should be noted that recrystallization is sufficient in many cases instead of the chromatography. When undistilled 5 is used, chromatography is usually necessary.

Decolorization of Dichloro Diels-Alder Adduct (1) The reagents tested are summarized in the discussion section of this thesis. (details of which are in lab notebook) However, by doing many experiments the best procedure to date is as follows. (based on t.i.c. and n.m.r. of reaction mixtures) A solution of 3.8g of magnesium dust and 0.5g of 6, in 20ml tetrahydrofuran, was stirred in round bottom flask at 54°C. Five drops of acetic acid are added at time=0 minutes. At time=15 minutes, one equivalent or 0.19g of iodine in 5ml of tetrahydrofuran is added, using a dropping funnel. Over a 15 minute period, the red iodine color should disappear and a fine light gray dust should be present. At time=45 minutes, 0.19g of iodine in 5ml of tetrahydrofuran is added using a dropping funnel. (again, a fine gray dust should appear after 15-30 minutes) The reaction should be monitored by t.i.c. and stopped after 2-3 hours. Immediately upon cooling, the reaction mixture should be passed through a 3" plug of dry silica gel to remove acid, magnesium, and magnesium salts. Tetrahydrofuran may now be removed under vacuum and the remaining yellow solid chromatographed on dried silica gel using 100 hexane/001 methylene chloride. Anthracene has Rs=0.60, 5 has Rs=0.38, and the product (1) has Rs=0.41. The hydrolyzed diketone comes off immediately after the anthracene (bright yellow) and trails, as would be expected due to hydrolysis on the column.
Dibis(trimethylsilyl)mercury\(^{9,13}\) The sodium amalgam was prepared by adding 1.92g (0.004mole) of sodium metal to 20ml of triple distilled mercury in a Parr hydrogenation bottle within a dry box. Then 9.42g (0.007mole) of trimethylsilyl chloride in 20ml of degassed (freeze-thawed with argon) cyclopentane was added to the Parr bottle, the bottle was sealed and clamped to a Parr hydrogenation apparatus and shaken for 7 days. Again, working in the dry box, the yellow organic phase was transferred by pressure through stainless steel tubing through a standard Schlenk filtration apparatus to yield a bright yellow solution. The solvent was removed under vacuum and 10g (+70\% yield) of bright yellow crystalline product remained. The m.p. was 99-102°C decomp. (lit.\(^9\) m.p. 102-104°C decomp.)

Monochloroethylene Carbonate (7)\(^{15}\) The procedure is straightforward, although, some details are not in the literature procedure. The light source is critical due to spectral distribution. I used a 250 watt ITT (infra-industrial) light bulb. The reaction can be followed by n.m.r. knowing: 1) ethylene carbonate-\(\Delta\) (singlet) at 4.52ppm; 2) monochloroethylene carbonate-\(\Delta\) (doublet of doublets) at 6.48ppm, 4.88ppm, and at 4.60ppm; 3) dichloroethylene carbonate-\(\Delta\) (singlet) at 6.30ppm

Vinylene Carbonate (9)\(^{13}\)

Dibromomethylene Carbonate (9)\(^{16}\)

Hexabromovinylene Carbonate (10)\(^{17}\) I have not been able to reproduce this literature procedure as discussed in the previous section. I would suggest the use of DMS and other dehalogenating reagents found in reference 18 and 20.
REFERENCES AND NOTES


6 - Ibid, pp. 1292

7 - Ibid, pp. 630

8 - J. J. Denoy, experimental result (notebook 1, pp. 12)


13 - D. P. Stack and R. M. Connect, unpublished results


16 - Ibid., 77, 3709(1955)

References and notes - (cont'd)

