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SYNTHESIS OF α-CHLOROBENZHYDRYL BENZYL SULFIDE AND SULFONE, AND THE IN SITU DECOMPOSITION OF THE SULFIDE INTO BENZOPHENONE BIS(BENZYLTHIO) ACETAL

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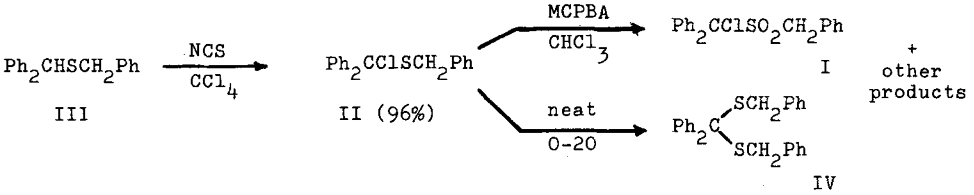
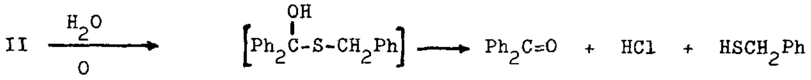
The synthesis of α-chlorobenzhydryl benzyl sulfone (I) was essential because it was the suspected primary intermediate in an unexpected and rapid rearrangement of benzhydryl benzyl sulfone on treatment with CCl_4-KOH.[2] The preparation of I from α-chlorobenzhydryl benzyl sulfoxide was aborted when attempted α chlorinations of benzhydryl benzyl sulfoxide with SO_2Cl_2 resulted in quantitative cleavage.[3] Synthesis of I directly from α-chlorobenzhydryl benzyl sulfide (II) was initially considered unpromising because of its expected instability, at least during oxidation.[4] Moreover, attempted α chlorination of benzhydryl benzyl sulfide (III) to II with SO_2Cl_2 also resulted in cleavage.

We have now quantitatively prepared II from III (with NCS) and have obtained I from II (with *m*-chloroperbenzoic acid). Both I and II were isolated and characterized; neither has been previously reported. Compound II is indeed unstable and formed benzophenone bis(benzylthio) acetal (IV) even when stored at 0° in a stoppered container. Likewise, products other than I were produced during oxidation.



Benzhydryl Benzyl Sulfide (III). For the subsequent reaction this sulfide was freshly prepared (neat, equimolar mixture of α-toluenethiol and benzhydryl chloride or bromide, 25°; 100% yield) and purified; mp 71-72° (from hexane; lit[5] mp 70-71); nmr δ^{CCl_4} 7.19, 7.15 (s, 15 H, Ph), 4,79 (s, 1 H, CH), and 3.46 (s, 2 H, CH_2).

α-Chlorobenzhydryl Benzyl Sulfide (II). An equimolar solution of III and NCS in CCl_4 was stirred at 0° for 6 hr. The precipitated succinimide was removed and the nmr spectrum of the colorless solution taken immediately indicated the presence only of II: δ^{CCl_4} 7.52 (m, 4 H, *o*-Ph_2C), 7.25 and 7.17 (m and s, 11 H, Ph), and 3.79 (s, 2 H, CH_2). Evaporation of the solvent left II as a very pale yellow oil, 96% yield. To confirm the structure of II, a weighed sample of the oil dissolved in CCl_4 was added to ice and the mixture stirred for 1 hr; the aqueous layer became very acidic (pH < 1). The CCl_4 layer was washed with dil KOH and evaporated leaving only benzophenone (> 95% yield). The aqueous layer, treated with HNO_3 and $AgNO_3$, provided >95% yield of AgCl.



$$\text{II} \xrightarrow[\text{0}]{\text{H}_2\text{O}} \left[\text{Ph}_2\overset{\text{OH}}{\overset{|}{\text{C}}}\text{-S-CH}_2\text{Ph}\right] \longrightarrow \text{Ph}_2\text{C=O} + \text{HCl} + \text{HSCH}_2\text{Ph}$$

α-Chlorobenzhydryl Benzyl Sulfone (I). A solution of freshly prepared II in $CHCl_3$ was stirred at 0-5° while 2 mol equiv of MCPBA was added over a 4-hr period. After being washed with aq $NaHCO_3$ the solution was concentrated to a pale yellow oil which slowly solidified. Chromatography on a basic-alumina column with pentane, 1:1 pentane-ether, ether, and $CHCl_3$ as the respective eluents provided colorless oils from the first two fractions and granular white crystals from the third, mp 127-128.5° (dec) after recrystallizations from CCl_4-pentane, $CHCl_3$-hexane, and cyclohexane, identified as I (42% yield): ir $\nu_{\text{max, cm}^{-1}}^{\text{Nujol}}$ 1312 and 1148, 1130 (s, SO_2 asym and sym str); nmr δ^{CDCl_3} 7.86 (m, 4 H, *o*-Ph_2C), 7.42 and 7.31 (m and s, 11 H, Ph), and 4.22 (s, 2 H, CH_2); *Anal.* Calcd. for $C_{20}H_{17}ClO_2S$: C, 67.42; H, 4.77; Cl, 9.83; S, 8.99. Found: C, 67.70; H, 4.93; Cl, 10.14; S, 9.13.

Material recovered from the $CHCl_3$ eluate, mp 202° (dec) was identified as benzophenone bis(benzylthio) acetal S,S-tetroxide (V) (10% yield) by comparison with an authentic sample (*vide infra*). Apparently V was derived from IV which was formed from II during the reaction, as illustrated below.

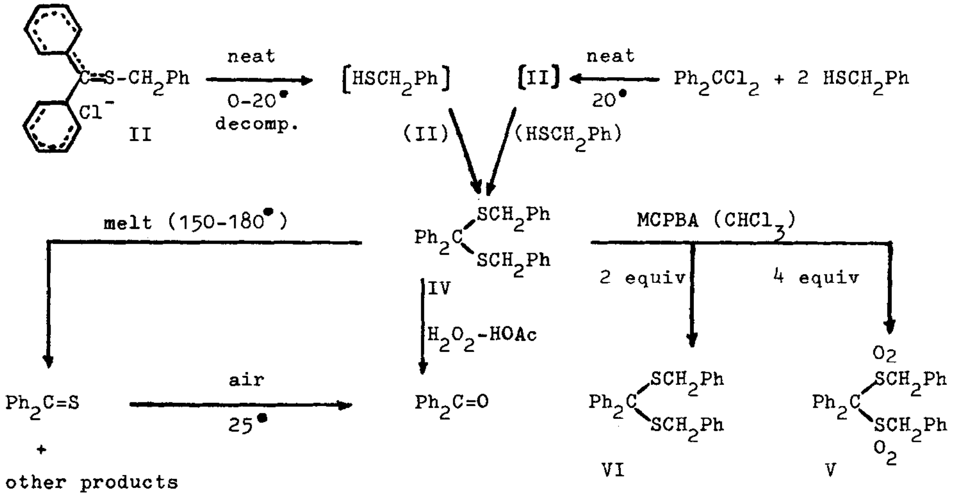
In Situ Decomposition of II. Formation of Bis(benzylthio) Acetal (IV). On standing in a stoppered flask at 0° or rm temp II underwent decomposition as was evidenced by the appearance of a new nmr singlet at δ 3.49 whose intensity increased with time concurrently with the formation of white microcrystals from the viscous oil (which had become pale blue-green). Trituration with pentane allowed easy separation of the crystals, mp 146-147° (from hexane-$CHCl_3$). Elemental analysis and mol wt determination suggested the assignment of structure IV which was verified by a comparison of ir and nmr spectra and mp with those of an authentic sample (*vide infra*). An abundance of hydrogen chloride was generated from II during the formation of IV, and the gradual appearance of a low-intensity singlet at δ 6.0 (CH) suggested the coformation of benzhydryl chloride. It is probable that the ion-pair character of II[4] and the presence of water vapor were responsible for this *in situ* decomposition.

Properties of IV. Compound IV was prepared directly (Ph_2Cl_2 + 2 $HSCH_2Ph$, neat[4] or in $CHCl_3$, 100% yield), mp 146-147° (from hexane-$CHCl_3$; lit[6] mp 144°); ir $\nu_{\text{max, cm}^{-1}}^{\text{Nujol}}$ 752, 735, 715 (sh), 709, 691 (all s); nmr δ^{CCl_4} 7.56 (m, 4 H, *o*-Ph_2C), 7.22 and 7.15 (m and s, 16 H, Ph), and 3.49 (s, 4 H, CH_2). These data are identical with those exhibited by the crystals formed from the decomposition of II.

When heated above its mp (150-180°) IV slowly becomes deep blue, indicative of the formation of thiobenzophenone.[7] When this procedure was carried out in a sealed tube, the blue-violet color persisted indefinitely even when the tube was refrigerated, an observation which reflects the characteristic resistance of thiobenzophenones, in contrast to other thiones, to undergo cyclic di- or trimerization.[8] However, when the blue oil was exposed to air (25°) the color was soon dissipated and benzophenone was identified as a major component of the residue, a result likewise expected of thiobenzophenone.[8]

The sensitivity of IV to cleavage reactions was also demonstrated during attempted oxidations (to V and VI) with H_2O_2-HOAc at 45°; benzophenone was quantitatively isolated. However, the desired disulfone (V) and disulfoxide (VI) were obtained by oxidation of IV with MCPBA in $CHCl_3$. The formation and reactions of IV are summarized in Scheme 1.

Scheme 1. Formation and Reactions of IV.



Benzophenone Bis(benzylthio) Acetal S,S,S',S'-Tetroxide (V). A solution of IV in $CHCl_3$ was stirred at 0° while 4 mol equiv of MCPBA was added during 1 hr, and stirring was continued at rm temp for an additional 8 hr. The mixture was washed with aq $NaHSO_3$ and $NaHCO_3$ and the solvent evaporated leaving white granular crystals, mp 204° (CCl_4; dec, evol of SO_2; lit[6] mp 204-208°); ir $\nu_{max,\ cm^{-1}}^{Nujol}$ 1328, 1312, and 1139, 1127 (s, SO_2 asym and sym str); nmr δ^{CDCl_3} 7.89 (m, 4 H, *o*-Ph_2C), 7.42 and 7.34 (m and s, 16 H, Ph), and 4.32 (s, 4 H, CH_2). These data are identical with those exhibited by the byproduct of the oxidation of II. The direct conversion of IV into V was quantitative.

Benzophenone Bis(benzylthio) Acetal S,S'-Dioxide (VI). To a stirred solution of IV in $CHCl_3$ at 0°, 2 mol equiv of MCPBA was added during 1 hr. After being refrigerated for several days then warmed to 30-40° for 2 hr, the mixture was washed with aq $NaHSO_3$ and $NaHCO_3$ and the solvent evaporated leaving an oil.

Dilution with pentane-Et$_2$O, and refrigeration, slowly afforded white crystal clusters, 10% yield (isolated); mp 101.5-102.5° (Et$_2$O-CHCl$_3$); ir $\nu_{max,}^{CCl_4}$ cm^{-1} 1074, 1055 (d, vs, S-O str; there was no O-S-O absorption); nmr δ^{CDCl_3} 7.80-7.00 (complex m, 20 H, Ph), 3.98 (d, *J* = 12.5 Hz, 2 H, 1 H of CH$_2$) and 3.38 (d, *J* = 12.5 Hz, 2 H, 1 H of CH$_2$).[9] These spectral data and a satisfactory elemental analysis confirmed the assignment of structure VI. The sharp melting point and lone methylene AB q exhibited by the isolated crystals are suggestive of one epimer, the *dl* or *meso*; a detailed characterization is now being undertaken.[10]

NOTES AND REFERENCES

1. This author gratefully acknowledges NSF (USA) Grant GF-36746, supplementary support from JSPS (Japan), and permission to use the facilities of the Sagami Chemical Research Center for a portion of this study.

2. Rearrangements of sulfones to alkenes on treatment with CCl$_4$-KOH-t-BuOH have been found to proceed via initial formation of the mono α-chloro sulfones.[a] While the initial formation of I, therefore, might likewise occur during the similar treatment of benzhydryl benzyl sulfone, the product isolated (triphenylethenesulfinic acid) was wholly unexpected.[b,c] As a result of this study the intermediacy of I in the latter reaction has been confirmed.[d] (a) C. Y. Meyers, L. L. Ho, G. J. McCollum, and J. Branca, *Tetrahedron Lett.*, 1843 (1973) and references therein; (b) W. S. Matthews, PhD Dissertation, Southern Illinois University-Carbondale, 1972; (c) C. Y. Meyers, U.S.-Japan Joint Seminar on Organosulfur Chemistry, Takarazuka, Sept. 1971, Abstracts pp 28-35; (d) C. Y. Meyers and W. S. Matthews, details to be published.

3. C. Y. Meyers and G. J. McCollum, *Tetrahedron Lett.*, 289 (1973).

4. Ion Pairing may be responsible for a number of unexpected results: e.g., in the oxidation of trityl phenyl sulfide, the condensation of benzenesulfinic acid with diphenyldichloromethane, etc. (C. Y. Meyers, M.-L. Hsu, W. S. Mattews, and G. J. McCollum, unpublished results.)

5. K. C. Schreiber and V. P. Fernandez, *J. Org. Chem.*, **26**, 2910 (1961).

6. T. Posner, *Chem. Ber.*, **35**, 2345 (1902).

7. See also A. Schönberg and O. Schütz, *ibid.*, **62B**, 2322 (1929), and ref 6.

8. Thiones have been reviewed by A. Ohno in "The Organic Chemistry of Sulfur," S. Oae, Ed., Plenum Press, London, in press, Chapter 5; E. Campaigne in "Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, New York, 1966, pp 917-959; E. Campaigne, *Chem. Rev.*, **39**, 1 (1946).

9. In either epimer (*dl* or *meso*) the two methylenes are themselves equivalent but possess nonequivalent protons (diastereotopic with respect to S-O); i.e., each epimer will exhibit a methylene AB quartet.

10. *Note added in proof:* Preliminary results have now been submitted for publication, C. Y. Meyers, L. L. Ho, A. Ohno, and M. Kagami, *J. Amer. Chem. Soc.*