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CLEAVAGE OF BENZHYDRYL BENZYL SULFOXIDE WITH SULFURYL CHLORIDE. EVIDENCE FOR THE GENERATION OF PHENYLSULFINE

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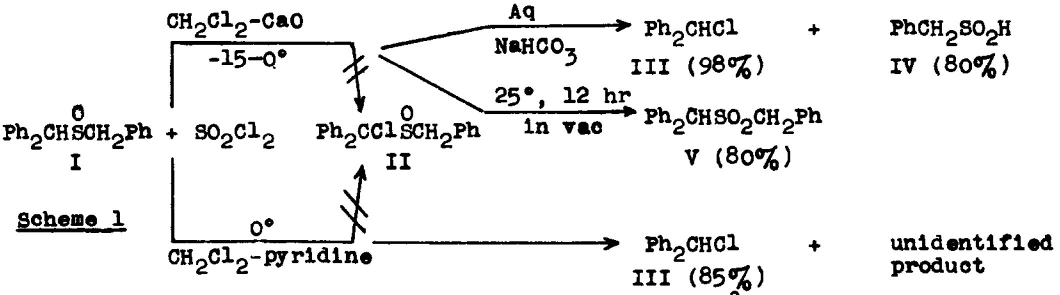
Recently Tin and Durst[1a] α-chlorinated eight sulfoxides (70-89%) with SO_2Cl_2 in CH_2Cl_2 containing CaO, while Tsuchihashi, et al.[2] prepared five α-chloro sulfoxides (67-84%) using this reagent in CH_2Cl_2 containing pyridine. The α-chlorination of sulfoxides with SO_2Cl_2, therefore, appeared to be general. Hoping to convert benzhydryl benzyl sulfoxide (I) into α-chlorobenzhydryl benzyl sulfoxide (II), we employed both procedures. However, in neither case was II detected at any stage during the reaction or workup. Instead, I was quantitatively cleaved under both conditions (Scheme 1): 1) In the presence of CaO the reaction afforded either benzhydryl chloride (III) and α-toluenesulfinic acid (IV) which were isolated when the solution was washed with aq $NaHCO_3$, or benzhydryl benzyl sulfone (V) which was isolated when the solution was concentrated and the residue kept under vacuum for 12 hr. 2) In the presence of pyridine the reaction provided III and an unidentified product.



Scheme 1

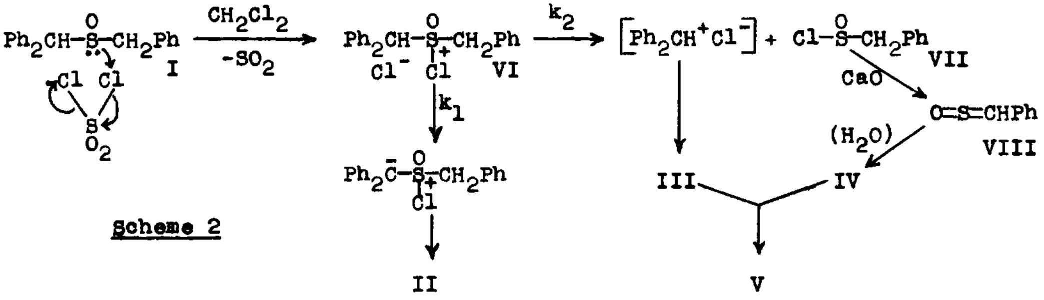
Preparation of I. Benzhydryl benzyl sulfide (mp 71-72°, lit[3] mp 70-71°) in HOAc at 15°, treated with an equiv of H_2O_2 over a 1-hr period, was converted into I (>90%): mp 129-129.5° (from benzene-pentane; lit[4] mp 125.5-126.5°); ir $\nu_{max,\ cm^{-1}}^{CS_2}$ 1059, vs, S-O str; nmr $\tau_{TMS}^{acetone\text{-}d_6}$ 2.20-2.70 (m, 15 H, Ph), 4.85 (s, 1 H, CH), 6.02 (d, J = 13 Hz, 1 H of CH_2) and 6.40 (d, J = 13 Hz, 1 H of CH_2).[5]

Reaction of I with SO_2Cl_2 in $CHCl_2$-CaO. To a mixture of 1.53 g (5.00 mmol) of I, 10 ml of CH_2Cl_2 and 3 g of CaO stirred vigorously at -15–0°, a solution of 0.67 g (5.00 mmol) of SO_2Cl_2 in 10 ml of CH_2Cl_2 was added dropwise. Within 15 min 35% of I was consumed, within 60 min all of I was consumed (nmr). The concentration of III increased with the consumption of I, but neither II nor V was detected. The mixture was filtered and the filtrate divided into two equal portions.

A. One portion was washed with aq $NaHCO_3$, dried ($MgSO_4$), and concentrated leaving 0.49 g (2.45 mmol, 98%) of III. Acidification of the aq washings produced a flocculent solid, IV, 0.31 g (2.00 mmol, 80%) mp 70-80° (lit[6] mp 64-69°, and[7] 61-63°, and[8] 59-60.5°), ir $\nu_{max}^{CS_2}$, cm^{-1} 1075-1085, vs, S–O str of SO_2H.[9] The odor of benzaldehyde was soon evident.[10] The identity of IV was confirmed by its conversion (CH_3I, aq $NaHCO_3$) into benzyl methyl sulfone, mp 125-126° (lit[10a] mp 127°) alone or mmp with an authentic sample.

B. The other portion was concentrated into a viscous oil which was held under vacuum overnight. The resulting solid was mainly V, 0.64 g (2.00 mmol, 80%) when crystallized from aq MeOH: mp 155-158°; mmp with authentic V (mp[11] 158-159.5°, lit[3] mp 153-154°) was not depressed. Spectra of the product and authentic V were identical: ir $\nu_{max}^{CS_2}$, cm^{-1} 1325, s, O-S-O asym str, and 1139, 1122, s, O–S–O, sym str; nmr $\tau_{TMS}^{acetone\text{-}d_6}$ 2.10-2.80 (m, 15 H, Ph), 4.33 (s, 1 H, CH), and 5.75 (s, 2 H, CH_2).

The possibility that II was an intermediate in the formation of III and IV is unlikely in view of the stability exhibited by similar α-chloro sulfoxides under these conditions[1a] or even in 30% aq NaOH.[12] Moreover, II could not have been the direct precursor of V since III was quantitatively formed long before V. Alternatively, cleavage prior to the formation of II would account for all the observations and is supported by related data. Scheme 2 is suggested:



Scheme 2

Durst and Tin[1b] presented evidence supporting the formation of chlorosulfoxonium salts like VI as required intermediates in reactions of sulfoxides with SO_2Cl_2. As suggested in Scheme 2, disposition of these salts might proceed by closely competitive reactions. abstraction of an acidic α proton (k_1 --leading to α-chlorination), and cleavage (k_2). With VI, formation of relatively stable Ph_2CH^+ would enhance the relative rate of cleavage so that $k_2 > k_1$. With other chlorosulfoxonium chlorides the two rates might be closer or their order reversed. Supporting this argument is the fact that Tin and Durst[1a] found that $PhCH_2\overset{O}{S}CH_3$ was an exception in their series, being α-chlorinated in only 25% yield. Moreover, they observed 71% α-chlorination of $(CH_3)_2CH\overset{O}{S}Ph$ but 89% for $CH_3CH_2\overset{O}{S}Ph$.[13] The extent of α-chlorination appears to increase with decreasing stability of the insipient carbonium ion, *viz.*, $Ph_2CH^+ > PhCH_2^+ > (CH_3)_2CH^+ > CH_3CH_2^+$, in accord with our proposal.[14]

α-Toluenesulfinyl chloride (VII), expected to be coformed with III,[14] was not detected. Direct conversion of VII into a Ca salt of IV is ruled out· such a salt should be insoluble in CH_2Cl_2 precluding the high yields of IV and V actually obtained, moreover, no Ca salts were found in the evaporated filtrate. On the other hand, rapid dehydrohalogenation of VII into phenylsulfine (VIII, thiobenzaldehyde S-oxide) in CaO-CH_2Cl_2 would be expected, based on the identical transformation in other alkaline media.[15b] Subsequently, VIII would be converted into IV by any H_2O present or generated (only 0.045 g, 2.50 mmol, was required), or into its Na salt by the addition of aq [illegible]CO_3. These reactions are consistent with the general formation and reactivity of sulfines.[15] This sequence, suggesting the intermediacy of a sulfine in the base-catalyzed hydrolysis of a sulfinyl halide into a sulfinic acid, parallels the base-catalyzed solvolysis of analogous sulfonyl halides in which the intermediacy of sulfenes has been proved.[16]

We have recently shown that neat mixtures of benzhydryl chlorides and sulfinic acids, held *in vacuo* at 25°, easily undergo condensation into the corresponding sulfones.[17] One example was the condensation of III with IV into V (100%), accounting for the formation of V in this study

Reaction of I with SO_2Cl_2 in CH_2Cl_2-Pyridine. Over a period of 10 min a solut[illegible] of 0[illegible] g (5.00 mmol) of SO_2Cl_2 in 10 ml of CH_2Cl_2 was added to a stirred solution of 1.53 g (5.00 mmol) of I and 2 g (25 mmol) of pyridine in 10 ml of CH_2Cl_2 held at 0°; the solution became bright yellow. An nmr spectrum taken when the addition was completed indicated that about 65% of I remained and 33% of III was already formed. A pair of doublets of very low intensity, $\tau_{TMS}^{acetone\text{-}d_6\text{-}pyridine}$ 5.01, J= 15 Hz and 5.60, J = 15 Hz,[5] suggested the presence of VII (about 4%) as a transient species. After being stirred at 0° for another 20 min the bright red solution was washed with dil H_2SO_4 then H_2O, dried, and concentrated (25°) to 1.43 g of a viscous red oil nmr $\tau_{TMS}^{acetone\text{-}d_6}$ 1.90 (m, 1 H), 2.50 (m, 15 H, 3 Ph), 3.67 (s, 1 H, $Ph_2\underline{CH}Cl$), no other resonances were exhibited, indicating the absence of I, II, V, and VII. The ir was identical to that of III but exhibited some additional bands at ν_{max}^{neat}, cm^{-1} 1695, m; 1330, vs; 1210, vs; 1144, s; 1121, s, 1046, m; 1015, m, and 877, m. No typical sulfoxide band (*ca.* 1060) was apparent. Moreover, neither IV nor V was isolated when the washed solution was treated as described previously (*cf*. CaO reaction).

The fact that II was not detected suggests that cleavage of VI was also responsible for the formation of III under these conditions (*viz.*, Scheme 2). Presumably, VII would be coformed and converted into VIII by pyridine.[15] However, neither IV nor V was isolated to reflect the formation of either precursor--contrary to the results produced with CaO. Since H_2O is not generated by the reactions with pyridine, and VIII similarly prepared from VII and Et_3N could not be isolated as the monomer[15b] (only monomeric S-oxides of thioketones and hindered thioaldehydes have been isolated),[15a] VIII could have formed and polymerized under these conditions. In the ylid form, primarily responsible for sulfine reactivity,[15b] the unhindered sulfine VIII would be especially vulnerable to pyridine-catalyzed polymerization. The nmr spectrum of the viscous oil supports this possibility, indicating an equimolar composition of III and a component whose empirical structure has one Ph and a deshielded proton. Assuming this component is polymerized VIII, the 1.43 g of isolated product represents 85% yields of III (0.85 g, 4.25 mmol) and VIII (0.58 g, 4.25 mmol).

NOTES AND REFERENCES

1. (a) K.-C. Tin and T. Durst, *Tetrahedron Lett.*, 4643 (1970); (b) T. Durst and K.-C. Tin, *Can. J. Chem.*, **49**, 2374 (1971).
2. G. Tsuchihashi, K. Ogura, S. Iriuchijima, and S. Tomisawa, *Synthesis*, 89 (1971).
3. K. C. Schreiber and V. P. Fernandez, *J. Org. Chem.*, **26**, 2910 (1961).
4. R. G. Hiskey and H. A. Harpold, *J. Org. Chem.*, **32**, 3191 (1967).
5. The diastereotopic methylene protons α to sulfinyl are sufficiently nonequivalent to exhibit mutual coupling.
6. J. L. Kice and R. H. Engebrecht, *J. Org. Chem* , **27**, 4654 (1962).
7. B. Holmberg, *Arkiv Kemi, Mineral., Geol.*, **14 A**, No. 8 (1940).
8. C. J. M. Stirling, *J. Chem. Soc.*, 3597 (1957).
9. L. J. Bellamy, "Infra-red Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1958, p 360.
10. Formation of benzaldehyde during the decomposition of α-toluenesulfinic acid was also observed by (a) E. Fromm and J deSeixas Palma, *Chem. Ber.*, **39**, 3308 (1906), (b) F. Kurzer and J. R. Powell, *J. Chem. Soc.*, 3728 (1952), and C. J. M. Stirling, ref 8.
11. Prepared in this laboratory by the oxidation of benzhydryl benzyl sulfide, W. S. Matthews, PhD Dissertation, Southern Illinois University, 1972.
12. R. N. Loeppky and D. C. K. Chang, *Tetrahedron Lett.*, 5415 (1968).
13. The corresponding cleavage products were not reported (ref 1a), but would have been lost during workup if not specifically sought.
14. Consistent with this proposal is the observation of D. L. Tuleen and T. B. Stevens, *J. Org. Chem.*, **34**, 31 (1969), that sulfides capable of cleavage into stable carbonium ions also undergo S-C scission instead of the usual α-chlorination with SO_2Cl_2. Similarly, they postulated that the reactions occur via the chlorosulfonium salt in addition to alkyl chlorides a sulfenyl chloride was isolated (*cf* VII; note that Tuleen did not use an alkaline medium).
15. (a) Sulfines have been reviewed by B. Zwanenburg and J. Strating, *Quart. Rept. Sulfur Chem.*, **5**, 79 (1970), and G. Opitz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967), (b) A. Majid Hamid and S. Trippett, *J Chem. Soc. (C)*, 1612 (1968)
16. (a) F. F. King and T. Durst, *J. Amer. Chem. Soc.*, **86**, 287 (1964); *ibid.*, **87**, 5684 (1965); (b) W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964).
17. C. Y. Meyers, M.-L. Hsu, W. S. Matthews, and G. J. McCollum, to be submitted.