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REARRANGEMENT OF BENZYLSULPHONYL CHLORIDE WITH TERTIARY AMINES: A ROUTE TO A LITTLE-KNOWN CLASS OF SULPHUR COMPOUNDS

J.F. King and T. Durst[1]

Chemistry Department, University of Western Ontario, London, Canada

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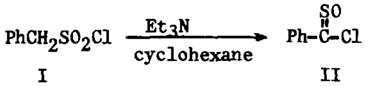
Sulphenes (RR'C=SO_2) though long virtually ignored by most chemists, have recently been discussed as intermediates in some newly-discovered reactions[2]. We have become interested in reactions involving sulphenes and oxythiones (RR'C=SO), and now wish to describe our study of an unusual reaction (I ⟶ II) which yields a stable oxythiono derivative, perhaps via a sulphene intermediate.



$$\underset{\text{I}}{PhCH_2SO_2Cl} \xrightarrow[\text{cyclohexane}]{Et_3N} \underset{\text{II}}{Ph\text{-}\overset{SO}{\overset{\|}{C}}\text{-}Cl}$$

In 1911 Wedekind and Schenk[3] reported that treatment of benzylsulphonyl chloride (I) with triethylamine gave *trans*-stilbene, sulphur dioxide, and triethylamine hydrochloride. To account for the formation of stilbene, these authors suggested the mechanism in Scheme 1.

$$2\ \underset{\text{I}}{PhCH_2SO_2Cl} \xrightarrow{Et_3N} 2\ \underset{\text{III}}{PhCH{=}SO_2} \longrightarrow 2\ PhCH\text{:} + SO_2 \longrightarrow PhCH{=}CHPh$$

Scheme 1

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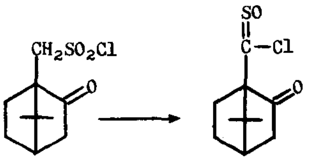
[1] Holder of National Research Council of Canada Scholarships, 1961-63.

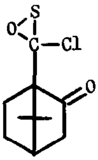
[2a] E. Henmo, P. de Mayo, A.B.M. Abdus Sattar and A. Stoessl, *Proc.Chem.Soc.* 1961, 238. [b] G. Stork and I.J. Borowitz, *J.Am.Chem.Soc.* **84**, 313 (1962). [c] G. Opitz and H. Adolph, *Angew.Chem.* **74**, 77 (1962). [d] W.E. Truce, J.J. Breiter, D.J. Abraham, and J.R. Norell, *J.Am.Chem.Soc.* **84**, 3030 (1962). [e] J.F. King, P. de Mayo, E. Morkved, A.B.M.A. Sattar and A. Stoessl, *Can.J.Chem.* **41**, 100 (1963). This paper also briefly lists earlier work on reactions believed to involve sulphenes.

[3] E. Wedekind and D. Schenk, *Ber.* **44**, 198 (1911).

In 1923 Wedekind et al. reported[4] an extension of the earlier work to camphor-10-sulphonyl chloride which with triethylamine or pyridine gave "camphorchlorosulphoxide". These authors showed that the chlorine, sulphur, and one of the oxygen atoms were attached (directly or indirectly) to C-10 and suggested structure IV, though alternative structures such as V were not excluded. Shortly afterward the analogous reactions were carried out on camphor-8-sulphonyl chloride[5], 3-bromocamphor-8-sulphonyl chloride[6] and camphor-8-sulphonyl bromide[7] but subsequently, except for mention in the abstracts and terpene literature the rearrangement of primary sulphonyl halides with tertiary amines (in the absence of other reagents) does not seem to have been further studied.



IV



V

We have reinvestigated these reactions and find in accord with Wedekind and Schenk's report that benzylsulphonyl chloride and triethylamine react either neat or in benzene solution to give stilbene (ca.30%) and also triethylammonium chloride and benzylsulphonate. In addition, a reddish-brown oily material with a band at 325 mμ in the ultraviolet and

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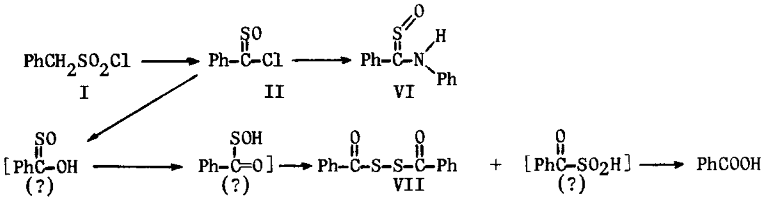
[4] E. Wedekind, D. Schenk and R. Stüsser, Ber. 56, 633 (1923).

[5] E. Wedekind and R. Stüsser, Ber. 56, 1557 (1923).

[6] H. Burgess and T.M. Lowry, J.Chem.Soc. 127, 271 (1925).

[7] T. Hasselström, Acta Acad. Sci. Fennicae A30, No. 12 (1930).

strong bands at 1145 and 1030 cm^{-1} in the infrared remained on evaporation of the mother liquor. When the reaction was carried out in ether (at 25^{o} or -60^{o}) a much higher yield of stilbene (63%) and none of the "red oil" was found. In cyclohexane solution, however, no stilbene was formed and only the "red oil" (corresponding to about 35% of I) together with triethylammonium benzylsulphonate (corresponding to about 60% of I) and triethylamine hydrochloride were obtained. Distillation of the "red oil" <u>in vacuo</u> followed by recrystallization from ether-petroleum ether gave II as yellowish-white plates, m.p. 38-39°. Calculated for C_7H_5SOCl: C, 48.7; H, 2.9; S, 18.5%. Found: C, 49.2; H, 3.2; S, 18.7%. The structure[8] (II) follows from (a) spectra, λ_{max} 234 mμ (ε 7750) and 323 mμ (ε 8800), ν_{max} 1145 cm^{-1} and 1030 cm^{-1}, and in the n.m.r. spectrum only a complex band around 7.5 p.p.m. from TMS; (b) hydrolysis with dilute hydrochloric acid yielded dibenzoyl disulphide (VII) and benzoic acid; and (c) reaction with aniline gave thiobenzanilide-S-oxide (VI) (see Scheme 2), which had previously been prepared by oxidation of thiobenzanilide with H_2O_2[9].



Scheme 2

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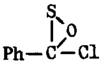
[8] Oxythiono compounds (e.g. II and VIII) suggest the interesting possibility of geometrical isomerism about the C=S bond. No indication of stereochemistry is intended in structure II. The position of the N-H stretching absorption in VI (3250 cm^{-1}) and its insensitivity to dilution is strongly suggestive of intramolecular hydrogen bonding, i.e. that the oxygen and nitrogen atoms in VI are <u>cis</u> to each other (as drawn).

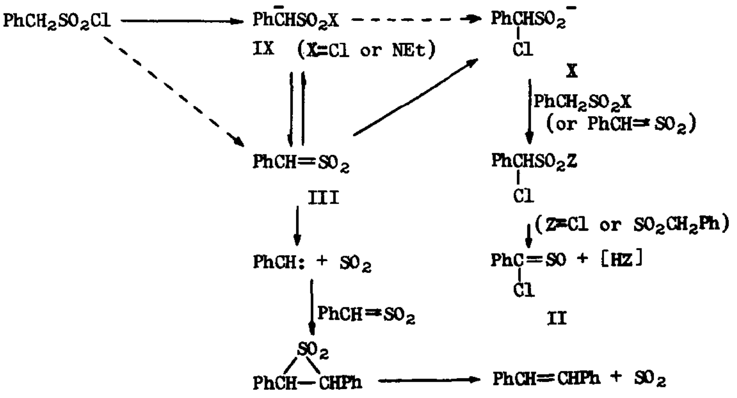
[9] W. Walter, J. Curtius, and H. Pawelzik, <u>Ann.</u> **643**, 29 (1961).

The structure of thiobenzanilide-S-oxide has been established by Walter's work[9] and also by studies in this laboratory which will be described in the full paper. Structure VIII, a conceivable alternative to II, is incompatible with the presence of the intense long-wavelength band in the ultraviolet spectrum.


VIII

We have also prepared the "camphorchlorosulphoxide" from camphor-10-sulphonyl chloride. The compound has strong infrared absorption at 1752, 1150, 1132 and 1052 cm^{-1} and shows in the n.m.r. spectrum only the geminal dimethyl, methylene and methine hydrogens expected on the basis of structure IV. The spectroscopic data, together with Wedekind's observations and the similarity of this reaction to that of benzylsulphonyl chloride, leave no doubt that Wedekind's structure (IV) is correct.

Among the numerous possible mechanisms to account for the formation of stilbene and oxythiobenzoyl chloride (II) from I, we put forward Scheme 3 as a working hypothesis.



Scheme 3

Any attempt to specify which step is most strongly affected by the changes in solvent would seem premature at this stage. Previous studies on reactions believed to involve sulphenes[2e] suggest that nucleophilic attack on sulphenes takes place more rapidly on the sulphur atom than on the carbon. (The reaction is thus analogous to nucleophilic attack on ketenes.) Under the conditions of this reaction, however, any nucleophilic attack (of Cl^- or NEt_3) on sulphur (to give IX) is reversible, whereas that on the carbon (to give the sulphinate ion (X)) may be essentially irreversible because of further reaction of X. It should be noted that the analogy with ketenes is only formal since nucleophilic attack on the non-carbonyl carbon of the ketene group gives a species of comparatively high energy relative to X. Further studies of the mechanism of these reactions are being carried out.

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