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A NEW SYNTHESIS OF SULFONYLNITRENES

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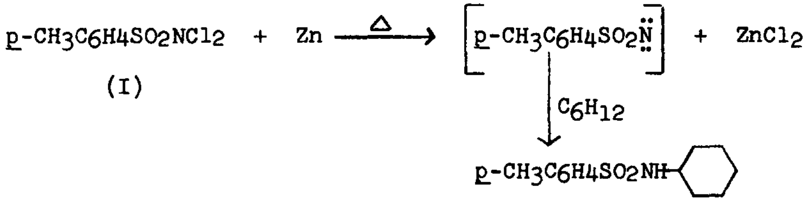
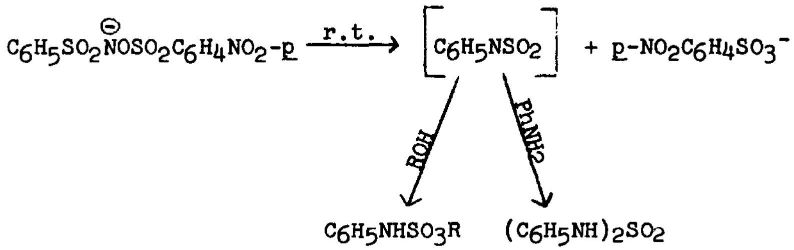
We have found that heating a solution of Dichloramine-T(I) in cyclohexane with zinc yields a sulfonylnitrene, which inserts into a C-H bond of the solvent.



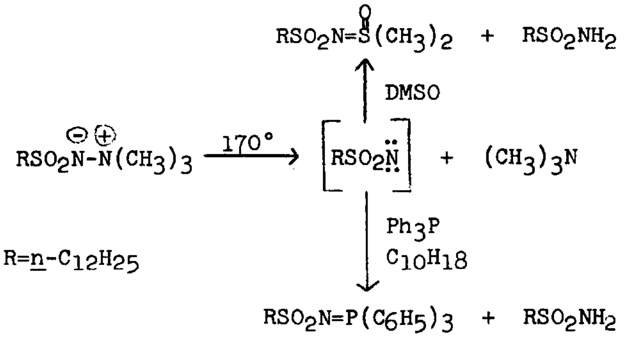
Several years ago Lwowski and Scheiffele (1) decomposed the triethylammonium salt of N-p-nitrobenzenesulfonoxybenzenesulfonamide in methanol, ethanol, and aniline and isolated products derived from a Lossen-type rearrangement to sulfurylaniline.



That the sulfurylaniline was not formed by rearrangement of a sulfonylnitrene intermediate was shown by carrying out the rearrangement in toluene—methylene chloride or in benzene; in neither case was there any indication of the formation of an anilide or toluidide, the products expected from a sulfonylnitrene in these solvents (2). Furthermore, there are no reports of benzenesulfonylnitrene rearrangement to sulfurylaniline (3).

Dermer and Edmison (6) reported that both Chloramine-T and benzenesulfonyl azide liberate nitric oxide from nitrobenzene on heating. However, no other products could be isolated from either reaction, and in this laboratory a number of salts of tosyl-N-chloramide were heated in cyclohexane with no evidence of any C-H insertion. Unfortunately, the low solubility of these salts in the reaction medium renders this negative evidence suspect; low yields in other nitrene reactions involving insoluble precursors have been reported (7).

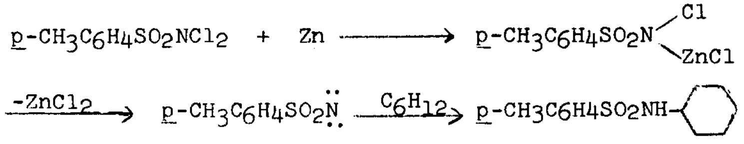
Very recently Robson and Speakman (8) reported the formation of a sulfonylnitrene by the thermolysis of an alkanesulfamidate, the nitrene reacting with DMSO to give a sulfoximine (9) and unsubstituted amide, and with triphenylphosphine in Decalin to give a phosphinimine and amide.



$$\begin{tikzcd} & RSO_2N{=}\overset{O}{S}(CH_3)_2 + RSO_2NH_2 \\ RSO_2\overset{\ominus}{N}\text{-}\overset{\oplus}{N}(CH_3)_3 \arrow[r, "170°"] & \left[RSO_2\ddot{N}\right] + (CH_3)_3N \arrow[u, "DMSO"'] \arrow[d, "Ph_3P \\ C_{10}H_{18}"'] \\ R{=}\underline{n}\text{-}C_{12}H_{25} & RSO_2N{=}P(C_6H_5)_3 + RSO_2NH_2 \end{tikzcd}$$

Although the formation of sulfonamide would appear to be a nitrene reaction, the products expected from a C-H insertion reaction, which we consider to be diagnostic for a nitrene intermediate (10), were apparently absent. Also surprising is the 48% yield of amide from the reaction in Decalin containing a small amount of triphenylphosphine, since we found little if any amide from the thermolysis of an alkanesulfonyl azide in an aliphatic hydrocarbon, a reaction which undoubtedly involves a nitrene intermediate.

A plausible scheme to explain the formation of nitrene from Dichloramine-T and zinc might be as follows:



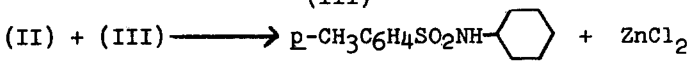
The reaction may have been successful because the intermediate chlorozinc derivative would be expected to be soluble in the reaction medium, whereas other Chloramine-T derivatives are insoluble. This could explain why the reaction failed when sodium was substituted for zinc. An alternative explanation, that tosyl-N-chloramide(II) is formed and undergoes α-elimination of hydrogen chloride, would seem to be ruled out, as would direct loss of chlorine, since in both cases sodium would be expected to give the same results as zinc.

$$\begin{tikzcd}
\underline{p}\text{-}CH_3C_6H_4SO_2NCl_2 \arrow[r, "C_6H_{12}"] \arrow[dr, "-Cl_2"'] & \underset{(II)}{\underline{p}\text{-}CH_3C_6H_4SO_2NHCl} + C_6H_{11}Cl \arrow[d, "-HCl"] \\
 & \underline{p}\text{-}CH_3C_6H_4SO_2\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}
\end{tikzcd}$$

Although we consider insertion into a C-H bond of a saturated hydrocarbon to be diagnostic for a nitrene intermediate, there is some possibility that this reaction followed a totally different course, e.g.,

$$\underline{p}\text{-}CH_3C_6H_4SO_2NCl_2 + C_6H_{12} \longrightarrow \underset{(II)}{\underline{p}\text{-}CH_3C_6H_4SO_2NHCl} + C_6H_{11}Cl$$

$$C_6H_{11}Cl + Zn \longrightarrow \underset{(III)}{C_6H_{11}ZnCl}$$



However, in view of the acidity of II the last step appears very unlikely.

In a typical experiment, a mixture of 5.0 g. of Dichloramine-T (11), 1.4 g. of zinc dust and 150 ml. of dry cyclohexane was refluxed with stirring for 21 hours. The resulting mixture was evaporated to dryness, and the residue was triturated with carbon tetrachloride. The carbon tetrachloride solution was filtered, extracted with 50 ml. of 5% aqueous sodium hydroxide, dried over magnesium sulfate and then evaporated to dryness. There remained 0.40 g. of a viscous oil which crystallized when seeded with authentic N-cyclohexyl p-toluenesulfonamide. Gas chromatographic analysis indicated that 80% of the product was N-cyclohexyl p-toluenesulfonamide. In a control experiment in which zinc was omitted only p-toluenesulfonamide was isolated.

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(3) Reichle (4) isolated a 17.5% yield of azobenzene from the vapor-phase pyrolysis of benzenesulfonyl azide at 625°, while Balabanov and coworkers (5) isolated trace amounts from decomposition in refluxing cyclohexanone. However, there is no evidence for the intermediacy of a nitrene in either reaction.

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