Tetrahedron Letters No.8, pp. 703-707, 1967. Pergamon Press Ltd. Printed in Great Britain.

A NOVEL REARRANGEMENT ATTENDING THE ADDITION OF SULFENES TO 1,3-BIS(DIMETHYLAMINO)-3-PHENYL-1-PROPENE

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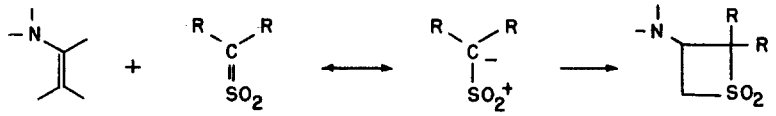
(Received 5 December 1966)

When a sulfene is generated in the presence of an enamine, a considerable propensity for cycloaddition to a β-aminothietane dioxide exists (1). The most obvious feature of this reaction is the ultimate bonding of the tetravalent sulfur atom of the sulfene to the



electron-rich β-carbon atom of the enamine system.

In an attempt to uncover new reactions of sulfenes, we have investigated the addition of such reaction intermediates to 1,3-bis(dimethylamino)-3-phenyl-1-propene (I). The unique structural feature of I which sets it apart from the customary α,β-unsaturated amines is the non-enamine benzylic tertiary nitrogen function at C-3 which, because of its inherent basicity and nucleophilicity, would be expected to compete favorably with the neighboring enamine system for the electrophilic sulfene. We now wish to describe a rearrangement reaction which does result from this new combination of structural characteristics.

1,3-bis(Dimethylamino)-3-phenyl-1-propene (I) was prepared by treating an ethereal solution of cinnamaldehyde with dimethylamine and powdered potassium carbonate under a nitrogen atmosphere with stirring for 24 hr. at ambient temperatures (2). Upon addition of methanesulfonyl chloride to a cold (approx. -15°) tetrahydrofuran solution of I and triethylamine, there was obtained by direct crystallization a 51% yield of II, m.p. 83° (3). Careful chromatography of the non-crystalline residue on neutral alumina permitted isolation of two additional crystalline solids, III, m.p. 91° (2-3%), and IV, m.p. 107-8° (3-4%) (3).

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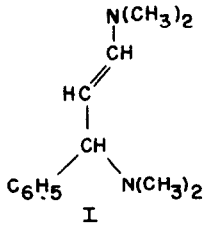
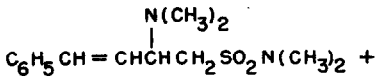
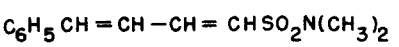


I

$\xrightarrow[(C_2H_5)_3N]{CH_3SO_2Cl}$ THF, −15°



II +



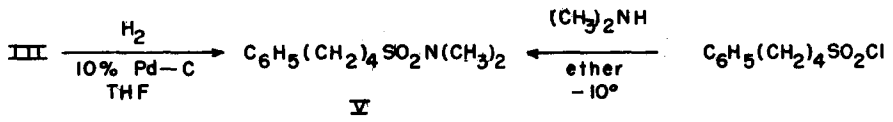
III +

IV

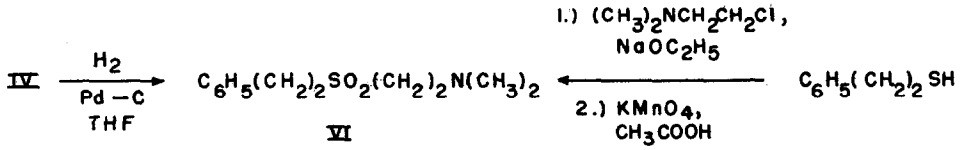
Initially, the molecular frameworks of II and III were shown to be similar. Chromatography of II on neutral alumina resulted in complete and quantitative conversion to III. Indeed, it was found that III is an artifact of the above reaction and arises because small quantities of II remain in the non-crystalline residue. The sensitivity of II to β-elimination upon chromatography is not unexpected.

The major component (II) was shown to be a sulfonamide because of its intense infrared absorption (in CCl_4) at 1330, 1150, and 970 cm.$^{-1}$ (4). Further, its principal ultraviolet absorption, λ_{max}^{EtOH} 251 mμ (ε 20,300) suggested the presence of a styrene chromophore (5). The n.m.r. spectrum, which was fully compatible with the structure proposed for II, displayed a low field singlet at δ 7.45 (5H, phenyl group), a complex multiplet in the 6.15 - 6.85 region (2H, vinyl protons), a complex absorption at 3.00 - 3.90 (3H), and singlets at 2.85 (6H) and 2.30 (6H) assignable to the methyl substituents of the sulfonamide and amino groups, respectively.

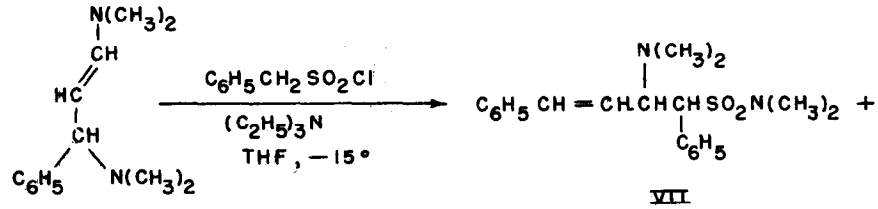
The presence of $C_6H_5CH{=}CH{-}CH{=}CH{-}$ grouping in III was derived from its ultraviolet spectrum which exhibited absorption in ethanol at 301 mμ (ε 38,700), a characteristic of the 1-phenylbutadiene chromophore (6). In addition, the complex n.m.r. spectrum of this material revealed the presence of nine low field (vinyl and aromatic) protons and the two methyl groups of the sulfonamide function (δ 2.75). The structures of II and III were firmly ascertained by catalytic hydrogenation of III to N,N-dimethyl-4-phenyl-1-butanesulfonamide (V), m.p. 48°, which was synthesized in unequivocal fashion from 4-phenyl-1-butanesulfonyl chloride (7) and dimethylamine.

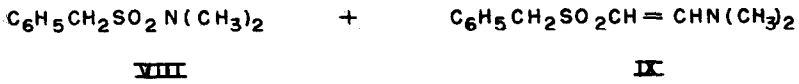


IV was defined as a styryl enaminosulfone on the basis of its infrared [$\nu_{max}^{CCl_4}$ 1640 (enamine), 1315 and 1110 cm.$^{-1}$ (sulfone)] and n.m.r. spectra (8). Confirmatory evidence was provided by catalytic hydrogenation to VI, which was independently synthesized by the condensation of β-phenethylmercaptan with β-dimethylaminoethyl chloride and subsequent permanganate oxidation of the resulting sulfide.



In similar fashion, the interaction of phenylmethanesulfonyl chloride and I in the presence of triethylamine led to the formation of VII, m.p. 146-7° (48%), VIII, m.p. 100-1° (22%) (9), and IX, m.p. 85° (3%) (10). The structure of compound VII was ascertained by

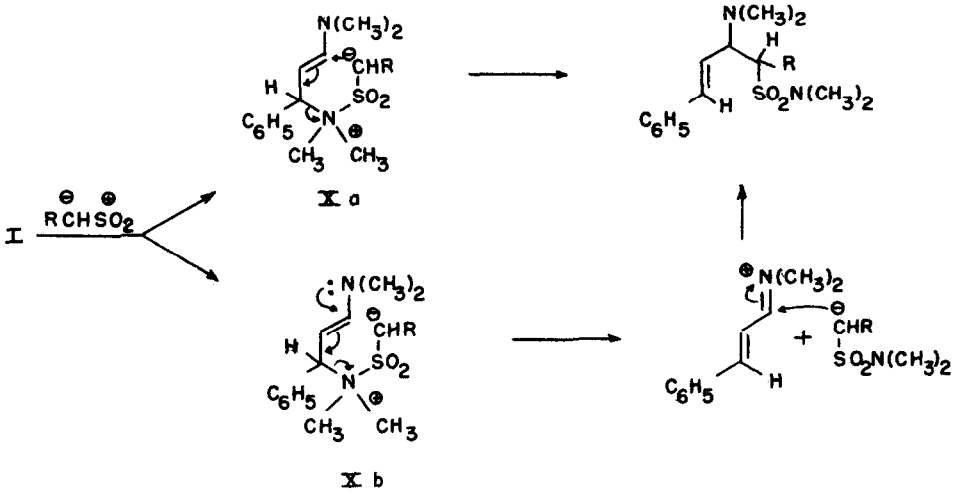




similar degradative and spectral evidence.

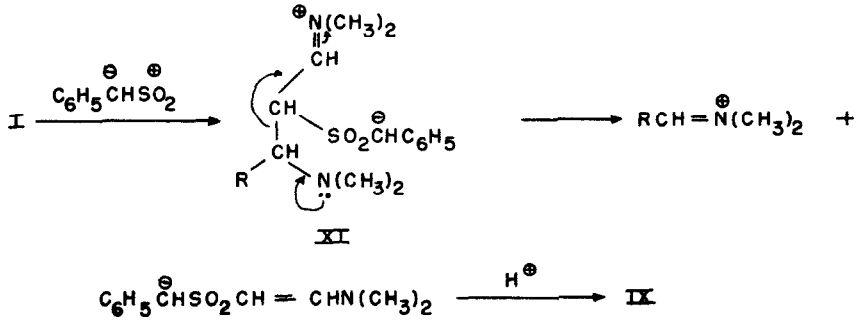
The genesis of II and VII can be derived in a mechanistically plausible fashion by invoking initial attack of the sulfene at the benzylic nitrogen atom. The conversion of the resulting dipolar species (X) to the rearrangement products can result either by the intramolecular attack of the nucleophilic α-sulfonyl carbanion at the α-position of the

enamine system with synchronous double bond migration and cleavage of the bond to positively-charged nitrogen (via six-centered transition state Xa) or by a cleavage-recombination



process (Xb). Contributing to the favorable energetics of this rearrangement is the fact that such a double bond migration leads to a conjugated styrene system.

The formation of IV can be attributed to a small amount of cycloaddition leading to a substituted 3-aminothietane which undergoes cleavage in the manner described earlier (11). Enaminosulfone IX can only arise by virtue of the fact that the cycloaddition of phenylsulfene to I is non-concerted. It is quite clear that IX should result irrespective of the nature of the substitution at R (in XI) and ancillary studies have verified this conclusion.



N,N-Dimethylphenylmethanesulfonamide (VIII) may find its origin in the protonation of the carbanionic moiety formed in the fragmentation of Xb.

The novel rearrangement just described suggests that the reactions of sulfenes need not be limited to 1,2-addition of protic molecules (12) and 1,3-dipolarophiles (13), nor to cycloaddition to electron-rich substrates (1), but may be quite unique and varied.

Acknowledgment. We are indebted to the National Science Foundation for generous support of this research.

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