

THE DOUBLE CYCLOADDITION AND ITS RELATED REACTION
OF SOME SULFENES TO KETENE DIETHYLACETAL OR MORPHOLINO-CYCLOHEXENE-1

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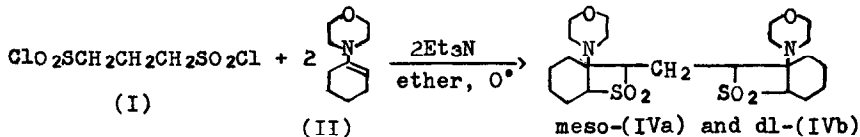
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It has recently been reported that alkanesulfonyl chlorides react with triethylamine in the presence of ketene diethylacetal¹ or enamines² to afford four membered cyclic sulfones (thiethane dioxides). These reactions have been formulated as involving the intermediacy of sulfene (RCH=SO₂). Alkanedisulfonyl chlorides, however, have not yet been studied, though the reactions are expected to result in the formation of the disulfene followed by an interesting double cycloaddition, the product being a bithiethane tetroxide.

In the preceding paper,³ the present authors have submitted a report on the possibility of disulfene formation as an intermediate and its polymerization reaction.

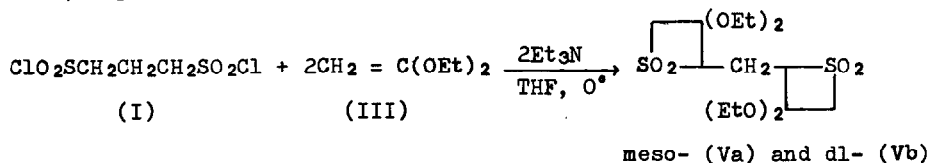
We now wish to report on the reaction of α,γ-propanedisulfonyl chloride (I) with triethylamine in the presence of morpholino-cyclohexene-1 (II) or ketene diethylacetal (III) to yield the corresponding bithiethane tetroxides (IV and V), though a similar reaction of α,β-propanedisulfonyl chloride (VI) with the same olefines led to only single cyclic sulfones (VII and VIII).

To the solution of II (0.1 mole) and triethylamine (0.1 mole) in diethyl ether (300 ml) was added slowly I (0.05 mole) in ether (150 ml) at 0° under stirring and was allowed to stand overnight. Extraction of the precipitates with hot benzene yielded a double cycloadduct (IV) in 19 % yield.



Recrystallization from methanol allowed the separation of IV into two isomers IVa, m.p. 206° (dec), needles; and IVb, m.p. 178-179° (dec), plates. IVa and IVb had the same NMR spectra: τ 5.75 (4H, multiplet, methine), 6.30 (8H, triplet, $-\text{CH}_2-\text{O}-$), 7.42 (8H, triplet, $-\text{CH}_2-\text{N}-$), 7.80 (2H, quartet, $-\dot{\text{C}}-\text{CH}_2-\dot{\text{C}}-$), and 8.32 (16H, multiplet, methylene protons of cyclohexane ring), and exhibited essentially the same IR spectra: 1310 ($\nu_{\text{as}}\text{SO}_2$) and 1140 cm^{-1} ($\nu_{\text{s}}\text{SO}_2$). The mass spectrum of IV was also in good agreement with the structure: peaks of $m/e=502$ (molecular ion), 416 ($M^+-86\{\frac{\text{O}}{\text{N}}\}$), and 352 (416-64[SO₂]) appeared in the spectrum, with major peaks at $m/e=207$, 180, 168, 167, 166, 165, 152, 136, 123, 110, 109, 108, 94, 91, 86, 81, 79, 78, 77, 67, 64, 57, 55, 44 and 41. (Found: C, 54.80; H, 7.87; N, 5.45; S, 12.53 for IVa and C, 55.00; H, 7.79 for IVb. C₂₃H₃₈N₂O₆S₂ requires: C, 54.95; H, 7.62; N, 5.57; S, 12.76 %.) On the basis of the solubility and m.p., IVa and IVb should correspond to meso- and dl- form respectively.

A similar reaction of I with triethylamine in the presence of III led to the formation of V in 23 % yield, which when recrystallized from ethanol and chromatographed over alumina using 1:1 CHCl₃-CCl₄ as the solvent yielded two isomers Va, m.p. 168-170°; and Vb, m.p. 129-136°.

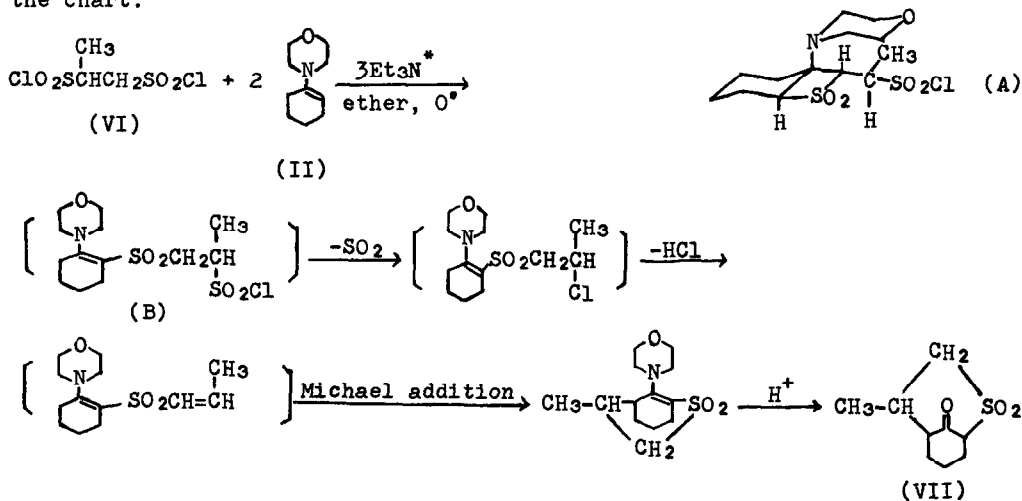


Confirmation of the structure of V was achieved in a manner paralleling that employed above for IV. NMR: τ 5.68 (2H, triplet, methine), 5.86 (4H, singlet, $-\text{SO}_2-\text{CH}_2-\dot{\text{C}}-$), 7.46 (2H, multiplet, $-\dot{\text{C}}\text{H}-\text{CH}_2-\dot{\text{C}}\text{H}-$), 6.52 (4H, quartet, $-\text{O}-\text{CH}_2-\text{CH}_3$) and 8.75 (6H, triplet, methyl). IR: 1320 ($\nu_{\text{as}}\text{SO}_2$) and 1140 cm^{-1} ($\nu_{\text{s}}\text{SO}_2$). (Found: C, 44.69; H, 7.12; S, 16.07 for Va and C, 44.82; H, 7.21; S, 15.96 for Vb. C₁₅H₂₀O₄S₂ requires: C, 44.98; H, 7.05; S, 16.01 %.)

The reactions of α,β -propanedisulfonyl chloride (VI) with triethylamine, however, did not result in the formation of a double cycloadduct but yielded monosulfones, VII (6 %) and VIII (13 %) under comparable reaction conditions that carried out for the disulfonyl chloride (I).

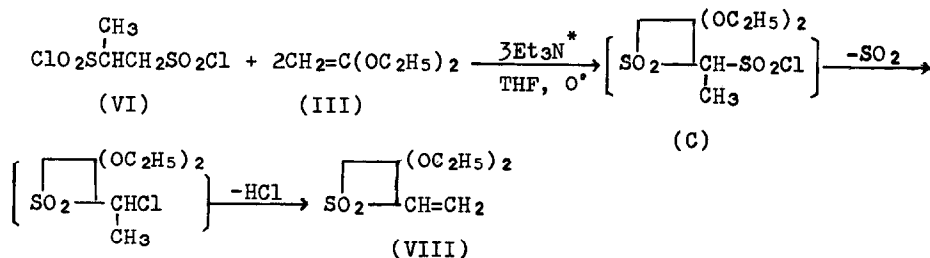
Structure VII was assigned on the basis of its NMR, IR, mass and elemental analyses. Its IR spectrum had a strong stretching frequency band at 1720 cm^{-1} and SO_2 stretching frequency bands at 1300 and 1120 cm^{-1} . The NMR spectrum displayed no vinyl protons, and exhibited doublet peaks at τ 8.78 (3H) assignable to methyl protons ($\text{CH}_3\text{-CH-}$), multiplet peaks at τ 7.0~8.53 (8H, methylene), 6.78 (1H), 6.62 (1H), and 6.30 (1H) (possibly assignable to methine protons of $\text{CH}_3\text{-CH-CH}_2\text{-}$, -CH-C- and $\text{-CH-SO}_2\text{-}$ respectively). The mass spectrum of VII was in good agreement with the structure: a molecular ion peak of $m/e=202$ appeared in the spectrum, with major peaks which corresponded to the fragments at $m/e=187$ ($\text{M}^+\text{-CH}_3$), 157 ($\text{M}^+\text{-CH}_3\text{-CH}_2\text{O}$), 123 ($\text{M}^+\text{-CH}_3\text{-SO}_2$), 129 (157-CO), 109 (157-SO), 81 (109-CO or 129-SO), 96 ($\text{M}^+\text{-C}_3\text{H}_6\text{-SO}_2$), 95 (96-H), 68 (96-CO), 67 (95-CO or 68-H), 55 ($96\text{-C}_3\text{H}_5$) and 41 ($67\text{-C}_2\text{H}_2$). Its elemental analysis revealed absence of nitrogen atoms. (Found: C, 53.66; H, 6.97; S, 16.15. $\text{C}_9\text{H}_{14}\text{O}_3\text{S}$ requires: C, 53.44; H, 6.98; S, 15.85 %.)

Compound VII most probably arises by substitution (compound B) instead of cyclization (compound A) because of the added steric interference by the methyl group, followed by the evolution of SO_2 and HCl prior to the Michael addition and the hydrolysis. The proposed course of these transformation is summarized in the chart.

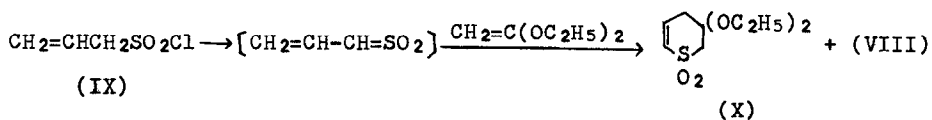


* Three moles of Et_3N were used to avoid the consumption of one mole of Et_3N due to $\text{Et}_3\text{N-SO}_2$ complex formation, though the experiments using two moles of Et_3N also resulted in the same products.

The cycloadduct VIII, m.p. 46.5~48° (lit.¹ 46~48°), was readily identified by comparison of its IR and NMR spectra with those of the authentic specimen synthesized by the reaction of ketene diethylacetal and allylsulfonyl chloride in the presence of triethylamine (Found: C, 48.89; H, 7.85; S, 14.40. Calcd. for C₉H₁₆O₄S: C, 49.07; H, 7.32; S, 14.56 %.)



The formation of VII or VIII should indicate the elimination of SO₂ from the intermediate (B) or (C) due to their instability, rather than from the disulfonyl chloride (VI). A supporting evidence of the route is that the 1,4-addition compound (X) was not found in the reaction mixture, though it should be expected¹ together with VIII if allylsulfonyl chloride (IX) formed first.



References

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- b. G. Opitz, H. Schempp and H. Adolph, *Ann. Chem.*, **684**, 92 (1965).
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