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REACTION OF TROPONE WITH MESYLSULFENE

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The relatively recent work by Opitz (1-4) on the generation and chemistry of mesylsulfene (II) and its stable trimethylamine adduct III prompts us to report our studies of the reaction

$CH_2{=}SO_2$ I

$CH_3SO_2CH{=}SO_2$ II

$CH_3SO_2\overset{-}{C}HSO_2\overset{+}{N}(CH_3)_3$ III

of tropone (5) with mesyl chloride and triethylamine. Dropwise addition (~1 hr) of a solution of purified triethylamine (33 mmoles) in anhydrous tetrahydrofuran to a stirred solution of tropone (10 mmoles) and mesyl chloride (30 mmoles) in anhydrous tetrahydrofuran at -5°C under nitrogen resulted in the immediate precipitation of triethylamine hydrochloride. Filtration followed by solvent removal afforded after several recrystallizations from acetone a white crystalline compound[**] in approximately 40% yield, m.p. 157-158°, Anal. Calcd. for $C_9H_{10}S_2O_5$: C, 41.21; H, 3.84; S, 24.45; mol. wt. 262. Found: C, 41.32; H, 3.97; S, 24.18; mass spectral data: $^m/e$ 262, 198, 184, 183, 182, 119, 118, 91, 90, 89, 79, 78, 77; osmometric mol. wt. in acetone 245; ν_{max}^{KBr} (cm^{-1}) 3050 (w), 2930 (m), 1660 (m), 1385 (s), 1375 (s), 1311 (s), 1220 (m), 1196 (s), 1169 (m), 1131 (s), 1121 (s); $\lambda_{max}^{C_2H_5OH}$ (mμ) 270 (2460); nmr (60 Mc, acetone-d_6) in ppm from tms, 6.10-6.75 (3H, complex multiplet), 5.96 (doublet, H_B, J_{AB} = 5.0 cps), 5.50 (quartet, H_C, J_{AC} = 4.0 cps, J_{CD} = 9.6 cps) 3.50-3.75 (complex multiplet, H_A), 3.46 (singlet, CH_3-).

The above data are clearly consistent with the apparent 2:1 sulfene-tropone adduct IV.

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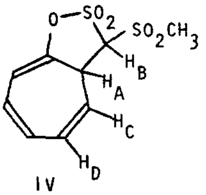
[**] This compound can also be sublimed at 100°C (0.05 mm).

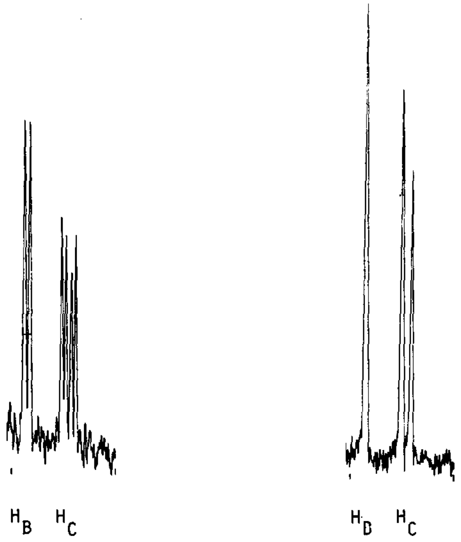


IV

Addition of a trace of solid Na_2CO_3 and a drop of D_2O to the nmr sample resulted in the complete disappearance of the doublet at 5.96 ppm as expected for the acidic hydrogen H_B.* Double resonance data at 100 Mc served as additional proof of structure IV. Irradiation at 360 cps (3.60 ppm, H_A) caused collapse of the doublet at 5.96 ppm (H_B) to a singlet as well as the quartet at 5.50 ppm (H_C) to a doublet, J_{CD} = 9.6 cps (see Fig. 1).

FIG. 1

DOUBLE RESONANCE DATA



NORMAL SPECTRUM

DECOUPLED SPECTRUM
IRRADIATE H_A

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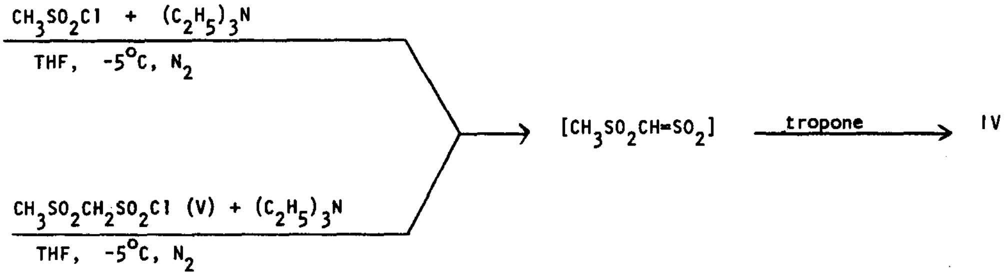
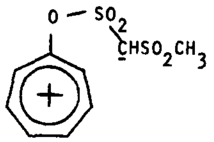
* The Hitachi RMU-6D mass spectrometer as well as the Varian A-60A nmr spectrometer used in this work were purchased through a National Science Foundation major equipment grant to Brown University.

In an effort to understand the nature of the attacking species (I or II) in the above transformation, the reaction of tropone with mesylmesyl chloride (V) (6) with triethylamine was investigated. Reaction of tropone (5.2 mmoles) and mesylmesyl chloride (5.2 mmoles) in tetrahydrofuran with triethylamine (5.7 mmoles) under nearly identical conditions as above afforded a white crystalline compound in approximately 32% yield, mp 157.5-159°, identical in all respects to the product of the reaction of tropone with mesyl chloride and triethylamine.



In view of the reported formation of II from either mesyl chloride in acetonitrile at -40°C or V in tetrahydrofuran at -70°C (2-4), the intermediacy of II in our findings appears quite probable. The formation of IV can be rationalized by initial nucleophilic attack of the tropone oxygen on the sulfene sulfur of II to give the dipolar species VI followed by ring closure.



VI

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