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CYCLOADDITIONS OF YNAMINES WITH SULFENES AND KETENES

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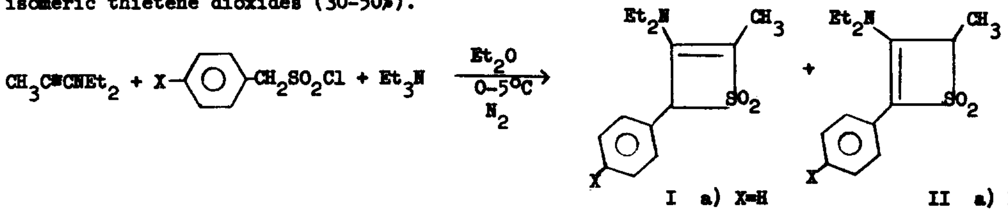
The reactions of sulfenes (generated in situ from alkanesulfonyl chlorides and triethylamine) with "electron-rich" olefins such as enamines[1,2], ketene acetals[3], ketene O,N-acetals, and ketene N,N-acetals[4] have been investigated extensively. Similarly ketenes react with like olefins such as enamines to give cycloadducts[5,6]. Since the related ynamines have been found to undergo cycloaddition reactions[7] with carbonyl compounds and their imines, 1,3-dipoles, and polar acetylenic and olefinic bonds, their reactions with sulfenes and ketenes were investigated and are reported herein.

Treatment of 1-diethylaminopropyne (Fluka) with several para-substituted phenylmethanesulfonyl chlorides in ether in the presence of triethylamine leads to the formation of a mixture of isomeric thietene dioxides (30-50%).[8]



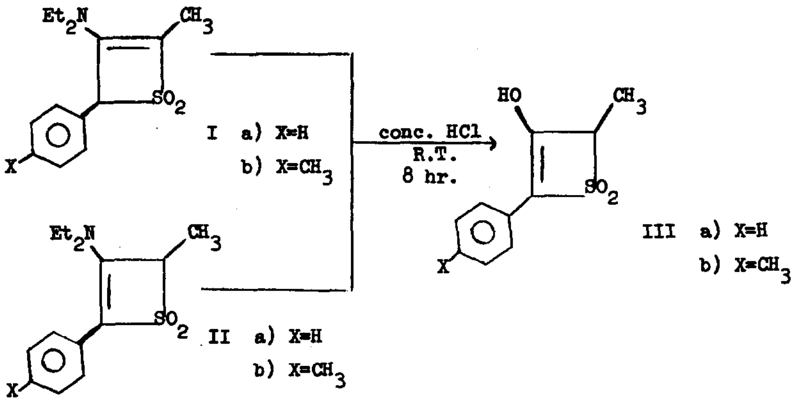
I a) X=H
b) X=CH_3
c) X=Cl

II a) X=H
b) X=CH_3
c) X=Cl

In a typical experiment, p-tolylmethanesulfonyl chloride (4.09 g, 0.02 mol) in 30 ml of ether is added to a solution of 1-diethylaminopropyne (2.22 g, 0.02 mol) and triethylamine (2.02 g, 0.02 mol) in 10 ml of ether at 0-5°. The white precipitate is filtered, washed with water to remove triethylamine hydrochloride, and recrystallized three times from 95% ethanol to give 2.3 g (41%) of a 3:2 mixture (by nmr) of 2-methyl-3-diethylamino-4-p-tolylthietene 1,1-dioxide (Ib) and 2-p-tolyl-3-diethylamino-4-methylthietene 1,1-dioxide (IIb), mp 110-111°. *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01; S, 11.48; MW, 279. Found: C, 64.73; H, 7.69; N, 4.90; S, 11.78; MW, 277.

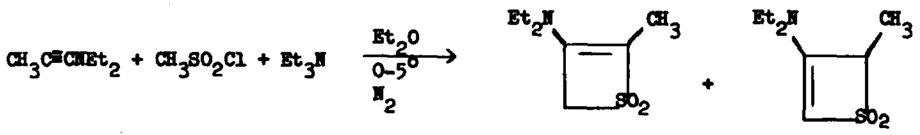
The products were identified from their ir, nmr, and mass spectra, and elemental analyses. The ir spectra of all the products showed bands at 6.1 μ (enamine), and 7.9 and 9.1 μ (sulfone). By repeated crystallization of the mixture of products from the phenylmethanesulfonyl chloride run, there was obtained unconjugated isomer Ia, mp 99-101°; nmr ($CDCl_3$): 0.85-1.2 δ (t, 6H), 2.0-2.1 δ (d, 3H), 2.85-3.3 δ (q, 4H), 5.5-5.7 δ (q, 1H), 7.3-7.4 δ (s, 5H). (The peculiar long range splitting across the ring has also been observed by Hasek, Meen, and Martin[9] in similar thietene 1,1-dioxides.) Isomer Ia was stable to dilute aqueous HCl, but in benzene solution in the presence of a trace of HCl it was transformed almost completely (> 96% by nmr) into the conjugated isomer IIa, mp 100.5-101.5°; nmr ($CDCl_3$): 0.85-1.2 δ (t, 6H), 1.6-1.8 δ (d, 3H), 2.95-3.35 δ (q, 4H), 4.4-4.8 δ (q, 1H), 7.25-7.4 δ (s, 5H).

Compounds I and II were converted to enols III in yields of ~70% by hydrolysis at room temperature with conc. HCl:



The enols were identified from their ir and nmr spectra, and elemental analyses. They also gave a positive test (deep purple coloration) with aqueous ferric chloride.

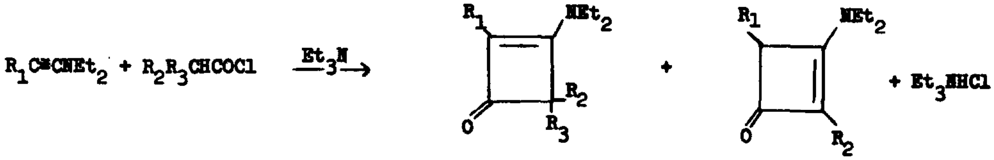
The reaction of methanesulfonyl chloride with 1-diethylaminopropyne in ether in the presence of triethylamine yielded a yellow oil, whose nmr spectrum indicated the presence of the two isomeric thietene 1,1-dioxides IV and V in a ratio of 1:1. However, all attempts to purify the products by recrystallization and distillation were unsuccessful. Work is now in progress to separate and purify the products by chromatography.



IV

V

Similar cycloadducts have also been obtained from the reactions of ketenes with ynamines. The ketenes, generated in the reaction solution from acid chlorides and triethylamine, were allowed to react with either 1-diethylaminopropyne or 1-diethylamino-2-phenylacetylene to give diethylaminocyclobutenones as illustrated below:



(where R_3=H)

Cycloadducts were obtained with:

R_1 = methyl; R_2 = phenyl, α-naphthyl; R_3 = hydrogen
R_1 = phenyl; R_2 = phenyl, α-naphthyl, methyl, hydrogen; R_3 = hydrogen
R_1 = phenyl; R_2 = phenyl; R_3 = ethyl

The reactions were generally successful in either pentane or ether at room temperature. However, it was necessary to carry out the reaction between 2-phenylbutyryl chloride and 1-diethylamino-2-phenylacetylene in refluxing hexane. Yields of cycloadducts were good (>50%) with aryl-substituted acetyl chlorides, but substantially lower with others. The products were identified from their ir and nmr spectra and elemental analyses.

In a typical experiment, phenylacetyl chloride (2.44 g, 0.016 mol) in 25 ml. of pentane is added to a solution of 1-diethylamino-2-phenylacetylene (2.5 g, 0.0145 mol) and triethylamine (2.04 g, 0.02 mol) in 50 ml. of pentane at room temperature. The white precipitate formed is washed with water to remove triethylamine hydrochloride and recrystallized from benzene-hexane to give a 57% yield of 3-diethylamino-2,4-diphenyl-2-cyclobutenone, mp 121-122°; nmr ($CDCl_3$): 0.9 δ (t, 6H), 3.2 δ (m, 4H), 4.5 δ (s, 1H), 7.3 δ (s, 10H); ir shows carbonyl absorption at 5.55 μ; Anal. Calcd for $C_{20}H_{21}NO$: C, 82.47; H, 7.22; N, 4.81; MW, 291; Found: C, 82.41; H, 7.25; N, 4.60; MW, 299.

Further work is under way to improve yields and determine the scope of these cyclizations.

Although there is also the possibility of forming cyclic enol ethers (as isolated by Kuehne and Sheeran[10]), we have not yet characterized any.

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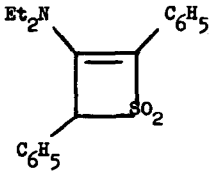

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