(2.1 g), ammonium carbonate (2.0 g), potassium cyanide (0.72 g in 5 ml of water), and 60% aqueous ethanol (35 ml) (reaction conditions—4 hr at 60°, 0.5 hr at 85°) gave at the expected point in the procedure 1.33 g (mp 181–187.5°, one zone on tlc) of crude 5-phenylhydantoin, whose ir accorded with pure material (our melting point of pure material was 186–187.5°).

B. Bucherer–Berg Reaction of Benzoin.—Employing benzoin (2.0 g) and prorated quantities of reactants as described above for benzil, there was obtained after 7.5 hr at 60° (then 0.5 hr at 85°) 1.72 g of crude solid (tlc two zones), which was separated by partitioning between ether and 2% alkali into benzoin (793 mg) and 5-phenylhydantoin (676 mg, mp 185–187.5°).

Registry No.—2a, 18749-95-6; 2b, 18744-13-3; 2c, 18749-96-7; 3-methyl-5-benzyl-5-phenylhydantoin, 4927-56-4.

Acknowledgments.—We wish to thank Dr. Thomas C. Butler, who supported this work and kindly provided several of the samples for the nmr study. We are indebted to Dr. C. G. Moreland (North Carolina State University) and to Mr. C. Fenske and J. Younger (Research Triangle Institute), who kindly measured nmr spectra.

Additions of Sulfenes to 1-Diethylaminopropyne

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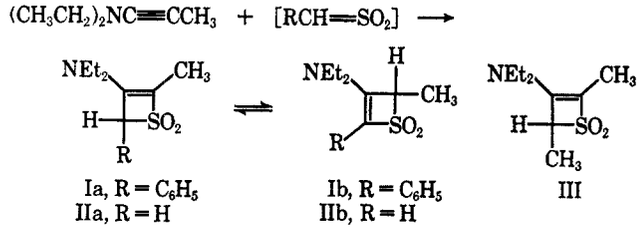
We wish to report the syntheses of three derivatives of 3-diethylaminothiete 1,1-dioxide from the addition of *in situ* generated sulfenes[1] to an ynamine. 3-Dialkylaminothiete 1,1-dioxides have been previously synthesized by sulfene cycloaddition to ketene O,N- and N,N-acetals.[2] Recently there have been three reports of thiete 1,1-dioxide syntheses by sulfene additions to a triple bond.[3]



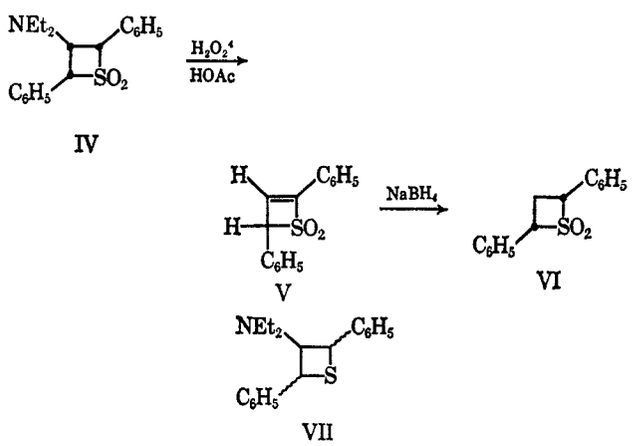
Ia, R = C_6H_5 Ib, R = C_6H_5 III
IIa, R = H IIb, R = H

Tautomeric mixtures of 2(4)-methyl-4(2)-phenyl-3-diethylaminothiete 1, 1-dioxides (Ia and Ib) and 2(4)-methyl-3-diethylaminothiete 1,1-dioxides (IIa and IIb), as well as 2,4-dimethyl-3-diethylaminothiete 1,1-dioxide (III) were obtained from the reactions of 1-diethylaminopropyne with the sulfenes generated *in situ* from toluene-α-sulfonyl chloride, methanesulfonyl chloride, and ethanesulfonyl chloride, respectively. Only the mixture of Ia and Ib has been successfully crystallized and separated into its tautomers; II and III are dark oils which have resisted all attempted methods of purification but whose spectral properties allow them to be easily characterized.

Attempted reductions of the carbon–carbon double bond in I, II and III with sodium borohydride were unsuccessful; only the starting materials could be recovered. Since it has been shown that a sodium borohydride reduction works on the thiete 1,1-dioxide ring system,[4] we assumed that the diethylamino group was in some way hindering the attempted reductions.

In an effort to test our hypothesis, 2,4-diphenylthiete 1,1-dioxide (V) was produced by oxidative deamination[5] of 2,4-diphenyl-3-diethylaminothietane 1,1-dioxide (IV) synthesized by the addition of *in situ* generated phenylsulfene to 1-diethylamino-2-phenylethene.[6] Indeed, sodium borohydride reduction of V proceeded smoothly to afford *cis*-2,4-diphenylthietane 1,1-dioxide (VI).[7]

Lithium aluminum hydride reduction of IV was attempted in an effort to produce the corresponding thietane (VII).[8] The reduction afforded a complex mixture from which only diethylamine has been identified. This is in accord with the implied assumption of Wells and Abbott[9] that the α proton on 2-phenyl-substituted thietane 1,1-dioxides is too acidic for hydride reduction of the sulfone. The failure of lithium aluminum hy-



(1) For a review of sulfenes, see G. Optiz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967).

(2) (a) R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **30**, 1495 (1965); (b) G. Opitz and H. Schempp, *Ann*, **684**, 103 (1965).

(3) Shortly after we submitted this Note we became aware of reports of three other groups who had independently performed additions of sulfenes to ynamines: A. M. Hamid and S. Trippet [*J. Chem. Soc., C*, 1612 (1968)] reported the addition of phenylsulfene to diethylphenylethynylamine. M. E. Kuehne and P. J. Sheeran [paper 0–74, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968] reported the formation of a four-membered ring from the condensation of a sulfene with an ynamine. W. E. Truce, R. H. Bavry, and P. S. Bailey, Jr. [*Tetrahedron Lett.*, 5651 (1968)] reported the addition of phenylsulfene to 1-diethylaminopropyne.

(4) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962).

(5). Method of L. A. Paquette and M. Rosen, *J. Org. Chem.*, **33**, 2130 (1968).

(6) Synthesized from the method of C. Mannich and H. Davidson, *Ber.*, **69**, 2106 (1936).

(7) Previously synthesized *via* another route by R. M. Dodson and G. Klose, *Chem. Ind.* (London), 450 (1963).

(8) (a) F. G. Bordwell and W. H. McKellin [*J. Amer. Chem. Soc.*, **73**, 2251 (1951)] reported the reduction of thietane 1,1-dioxide to thietane with lithium aluminum hydride. (b) G. Opitz, H. Schempp, and H. Adolph [*Ann.*, **684**, 92 (1965)] reported the lithium aluminum hydride reduction of 2-propyl-3-morpholino-1,1-dioxide to the corresponding thietane in 51% yield.

(9) J. N. Wells and F. S. Abbott [*J. Med. Chem.*, **9**, 489 (1966)] have suggested only that the 2-phenyls seem to hinder the hydride reduction.

dride to reduce 2-phenyl-substituted thietane 1,1-dioxides has also been observed by Truce and Norell.[10]

Experimental Section[11]

2(4)-Methyl-4(2)-phenyl-3-diethylaminothiete 1,1-Dioxide (I).—A solution of 5.5 g 0.05 mol) of 1-diethylaminopropyne (Fluka AG), 5.5 g (0.055 mol) of triethylamine (dried by distillation over calcium hydride), and 75 ml of anhydrous dioxane was placed in a 250-ml flask fitted with a reflux condenser, an inlet tube for nitrogen, and a dropping funnel. The flask was cooled by an ice–water bath, stirred magnetically, and flushed continuously with dry nitrogen. A solution of 9.5 g (0.05 mol) of toluene-α-sulfonyl chloride in 30 ml of anhydrous dioxane was added dropwise over a period of about 25 min. Filtration after 36 hr standing afforded triethylamine hydrochloride which was washed with several portions of dioxane. The washings were combined with the filtrate and the mixture evaporated on a rotary evaporator at aspirator pressure to give a dark oil. The oil was crystallized from methanol at $-10°$ to afford 7.0 g (0.027 mol, 54%) of large white crystals, mp 90–93°, after four recrystallizations from methanol, mp 109–110°. The nmr ($CDCl_3$) of this sample indicated that it was a mixture of Ia and Ib.

A second synthesis yielded an initial product, mp 110–114°, after six recrystallizations from methanol: mp 123–124°; λ_{max}^{EtOH} 200 mμ (ϵ 17,400) and 244 (11,300); ν_{max} ($CHCl_3$) 2990, 1650, 1430, 1270, 1185, 1150, and 1084 cm^{-1}; nmr ($CDCl_3$) δ 1.0 (triplet, 6 H, J = 7.0 Hz), 2.05 (doublet, 3 *H*, J = 1.8 Hz, 2-methyl), 5.65 (quartet, 1 H, J = 1.8 Hz, 4-H), and 7.4 (singlet, 5 H, 4-phenyl). The nmr spectrum clearly indicates structure Ia. During an attempted sodium borohydride reduction of this sample, Ia was equilibrated with a solution of 5 ml of 10% aqueous sodium hydroxide in 100 ml of methanol. The solution was neutralized with dilute aqueous sulfuric acid, evaporated to dryness, and the product (Ib) extracted with ethyl acetate and recrystallized: crude mp 86–89°; nmr ($CDCl_3$) δ 1.05 (triplet, 6 H, J = 7.0 Hz), 3.2 (quartet, 4 H, J = 7.0 Hz), 1.7 (doublet, 3 H, J = 7.0 Hz, 4-methyl), 4.7 (quartet, 1 H, J = 7.0 Hz, 4-H), and 7.4 (singlet, 5 H, 2-phenyl).

Anal.[12] Calcd for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22; N, 5.28; S, 12.08. Found: C, 63.41; H, 7.45; N, 5.18; S, 12.02.

2(4)-Methyl-3-diethylaminothiete 1,1-Dioxide (II).—The sulfene addition was performed with the method described above. The addition of a dioxane solution of 5.5 g (0.05 mol) of methanesulfonyl chloride to a dioxane solution of 5.5 g (0.05 mol) of 1-diethylaminopropyne (Fluka AG) containing 5.5 g (0.055 mol) of triethylamine afforded 6.7 g (0.036 mol, 71%) of a brown oil. Crystallizations were attempted from methanol, ethanol, chloroform, and combinations of ether and pentane with the previously mentioned solvents. The oil was dissolved in 10% aqueous sodium hydroxide and slowly removed from the solution by the addition of acid. A vacuum distillation (0.1 mm) at 150° was attempted, but only solvents could be distilled. The remaining product was used for all of the following spectral data: ν_{max} (neat) 2960, 1715 (apparent impurity), 1630, 1600, 1430, 1370, 1258, 1155, 1090, and 840 cm^{-1}. The nmr ($CDCl_3$) spectrum of this sample displays the peaks of both IIa and IIb. The ethyl groups' triplets are superimposed at δ 1.2 (J = 7.0 Hz), but the quartets are slightly offset (2.0 Hz) from one another such that they appear to be a "split" quartet (J = 7.0 and 2.0 Hz) at 3.2; the 2-methyl group of Ib appears as a triplet (J = 1.8 Hz) at 1.9 because it is split across the ring by the 4-H's, which appear as a quartet (J = 1.8 Hz) at 4.65; the 4-methyl of IIb, on the other hand, appears as a doublet (J = 7.0 Hz) at 1.6 as it is split by its adjacent 4-H, which appears as a quarter (J = 7.0 Hz) at 4.65; the 2-H of IIb appears unsplit at 5.15.

2,4-Dimethyl-3-diethylaminothiete 1,1-Dioxide (III).—The sulfene addition was performed with the method described above. The addition of a dioxane solution of 46.0 g (0.36 mol) of ethanesulfonyl chloride to a dioxane solution of 40.0 g (0.36 mol) of 1-diethylaminopropyne (Fluka AG) containing 40.0 g (0.39 mol) of triethylamine and work-up afforded a dark oil which resisted crystallization much like the above. The impure product was isolated as 64.0 g (0.31 mol, 86%) of a dark oil: ν_{max} (neat) 2960, 1725 (apparent impurity), 1625, 1430, 1375, 1259, 1200, 1093, and 765 cm^{-1}; nmr ($CDCl_3$) δ 1.15 (triplet, 6 H, J = 7.0 Hz), 3.3 (quartet, 4 H, J = 7.0 Hz), 1.87 (doublet, 3 H, J = 2.0 Hz, 2-methyl split by the 4-H), 1.9 (doublet, 3 H, J = 2.0 Hz, 4-methyl split by the 4-H), and 4.55 (16-line pattern, 1 H, J = 7.0 and 2.0 Hz, 4-H split by both methyls).

2,4-Diphenyl-3-diethylaminothietane 1,1-Dioxide (IV).—The sulfene addition was performed with the method described above. The addition of a dioxane solution of 38.0 g (0.20 mol) of toluene-α-sulfonyl chloride to a dioxane solution of 35.0 g (0.20 mol) of 1-diethylamino-2-phenylethene[6] containing 20.0 g (0.21 mol) of triethylamine and work-up afforded 65.0 g of a pale brown oil. Half the oil was used for the peracetic acid oxidative deamination. Crystallization of the other half from chloroform–ether afforded 17.0 g (0.07 mol, 70%) of nearly white crystals, mp 79–81°, and, after four recrystallizations from chloroform–ether, white crystals: mp 81.5–83°; λ_{max}^{EtOH} 226 mμ (ϵ 20,200); ν_{max} ($CHCl_3$) 2980, 1492, 1450, 1318, 1162, 1132, and 690 cm^{-1}; nmr ($CDCl_3$) δ 0.75 (triplet, 6 H, J = 7.0 Hz), 2.45 (quartet, 4 H, J = 7.0 Hz), 5.25 (doublet, 2 H, J = 9.0 Hz, 2-H and 4-H), 4.15 (triplet, 1 H, J = 9.0 Hz, 3-H), 7.45 (complex multiplet, 10 H, aromatic). It can be rationalized that the phenyls are *cis* because the 2-H and 4-H are each split equivalently by the 3-H. The Karplus equation[13] predicts a 9.0-Hz splitting for a dihedral angle of 12°. Puckering of the four-membered ring can account for a dihedral angle of 12°; thus all three protons are on the same side of the ring.

Anal. Calcd for $C_{19}H_{23}NSO_2$: C, 69.26; H, 6.99; N, 4.26. Found: C, 69.30; H, 7.02; N, 4.26.

2,4-Diphenylthiete 1,1-Dioxide (V).—A solution of 23.0 g (approximately 0.07 mol) of the oil from the reaction of 1-diethylamino-2-phenylethene with phenylsulfene (above), 64 ml of acetic acid, and 64 ml of acetic anhydride was stirred magnetically on an ice bath with slow addition of 25 ml of 30% hydrogen peroxide. The reaction was quite exothermic. After 12 hr, the color of the solution had changed from light brown to pale yellow and a precipitate of white crystals had formed, mp 131–133°, and, after four recrystallizations from chloroform: mp 133–134°; λ_{max}^{EtOH} 257 mμ (ϵ 17,400); ν_{max} ($CHCl_3$) 3030, 1492, 1450, 1310, 1157, and 864 cm^{-1}; nmr ($CDCl_3$) δ 6.1 (doublet, 1 H, J = 2.0 Hz, 3-H), 7.1 (doublet, 1 H, J = 2.0 Hz, 4-H), and 7.2–7.6 (complex multiplet, 10 H, aromatic).

Anal. Calcd for $C_{15}H_{12}SO_2$: C, 70.31; H, 4.69; S, 12.50. Found: C, 69.57; H, 4.68; S, 12.30.

Although this analysis is inconclusive for carbon, compound VI may be considered a derivative.

***cis*-2,4-Diphenylthiete 1,1-Dioxide (VI).**—A suspension of 3.8 g (0.016 mol) of V in 70 ml of ethanol was magnetically stirred under nitrogen. To this was added a solution of 1.9 g (0.05 mol) of sodium borohydride in 10 ml of 0.2% sodium hydroxide and resulting solution stirred for 45 min. The color of the solution changed from white to yellow, and it was cooled in an ice bath and acidified with dilute sulfuric acid to pH 6. All solvents were then evaporated on a rotary evaporator at aspirator pressure, and the remaining white precipitate of boric acid and product was sequentially extracted with ethyl acetate and chloroform. Evaporation of the chloroform left a white solid: yield 2.5 g (0.0097 mol, 67%); mp 161–162° (lit.[7] mp 163–164°); λ_{max}^{EtOH} 226 mμ (ϵ 20,200); ν_{max} ($CHCl_3$) 3030, 1493, 1450, 1410, 1175, and 1135 cm^{-1}; nmr ($CDCl_3$) δ 5.4 (two doublets, 2 H, 2-H and 4-H), 2.25 (complex multiplet, 2 H, 3-H's), and 7.4 (singlet, 10 H, aromatic). The *cis* configuration of VI was determined from the nmr spectrum; the benzyl protons at δ 5.4 are clearly split twice; *i.e.*, they are split by each proton in the 3 position and appear as a pair of doublets. The protons in the 3 position, however, are not magnetically equivalent; they are split by each other in addition to being split by the benzyl protons.

Anal. Calcd for $C_{15}H_{14}SO_2$: C, 69.77; H, 5.43; S, 12.40. Found: C, 69.55; H, 5.67; S, 12.23.

Registry No.—Ia, 18742-08-0; Ib, 17691-95-1; IIa, 17691-94-0; IIb, 17691-96-2; III, 18742-12-6; IV, 18744-25-7; V, 18744-26-8; VI, 18744-27-9; 1-diethylaminopropyne, 4231-35-0.

(10) W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3236 (1963).

(11) All melting points are corrected.

(12) Analysis reported is that of Ia, mp 123–124°.

(13) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).