chemical shifts of these four indoles were assigned using techniques described earlier in this paper.

The quality of the predictions appear to be good to excellent. For 2,7-dimethylindole, the difference between the predicted and observed values is only about 0.1 ppm, except at C-9 where the difference is somewhat greater but still less than 1.0 ppm. This could be expected to provide a favorable case because the two methyl groups are not close to one another and their mutual interactions should be small.

With the 1,2- and 2,3-dimethylindoles, the 1,2-methyl interactions should be roughly the same and as a result the deviations from the predicted shifts should be about the same. This is apparent from the resonance of C-2 which is upfield for both compounds by 2.0 ppm from what is predicted. The C-2 shift may be the result of methyl–methyl repulsions causing slight lengthening of the 1,2-ring bond in 1,2-dimethylindole and the 2,3-ring bond in 2,3-dimethylindole.[7] There is also an upfield shift at C-9 for both compounds, possibly because the methyl–methyl repulsions deform the five-membered ring with resultant lengthening of the 1,9 bond.

The worst agreement between prediction and experiment is seen for 2,3,5-trimethylindole. The previously discussed effects at C-2, C-3, and C-9 are present in about the same magnitude but the resonances at C-4 and C-6 show rather large unexplained deviations from prediction. These may be connected with the abnormalities of 5-methylindole itself as discussed above.

Experimental Section

The indoles used in this study were commercial materials and were used without further purification.

The chemical shifts were measured using the digital frequency sweep spectrometer[4a] with pseudo-random, noise-modulated, proton decoupling[6a] as previously described. The samples were dissolved in dioxane, usually at concentrations of 1.0 g/1.5 ml at which it was usually only necessary to average 10 to 15 scans to obtain adequate signal-to-noise ratios. Sweep rates of 2- or 4-Hz/sec at 50- or 100-Hz sweep widths were generally employed. The peak widths were usually on the order of from 1 to 3 Hz. The off-resonance, proton-decoupled spectra usually required 30 to 40 time-averaged scans although it was possible in most cases to identify the quaternary carbons after 10 to 15 scans.

Registry No.—Indole, 120-72-9; 1-methylindole, 603-76-9; 2-methylindole, 95-20-5; 3-methylindole, 83-34-1; 4-methylindole, 16096-32-5; 5-methylindole, 614-96-0; 6-methylindole, 3420-02-8; 7-methylindole, 933-67-5; 1,2-dimethylindole, 875-79-6; 2,3-dimethylindole, 91-55-4; 2,7-dimethylindole, 5621-13-6; 2,3,5-trimethylindole, 21296-92-4.

Diazo Alkane Adducts of Thiete Sulfone (Thiacyclobutene 1,1-Dioxide) in Synthesis of Thiabicyclopentane Dioxides, Pyrazoles, and Tetrahydrothiophene Sulfones[1-3]

DONALD C. DITTMER AND ROBERT GLASSMAN

Department of Chemistry, Bowne Hall, Syracuse University, Syracuse, New York 13210

Received August 18, 1969

Diazoalkanes have been added to the double bond of thiete sulfone (thiacyclobutene 1,1-dioxide) to yield 1- or 2-pyrazolines. Adducts of diphenyldiazomethane or methylphenyldiazomethane lose nitrogen on heating or on irradiation with ultraviolet light to give 2-thiabicyclo[2.1.0]pentane 2,2-dioxides. In contrast, the adducts of phenyldiazomethane and *p*-methoxyphenyldiazomethane lose sulfur dioxide to give pyrazoles. A route to thiophane (tetrahydrothiophene) sulfones from the thiabicyclopentane sulfones is shown.

Thiete sulfone has a reactive double bond; it and substituted thiete sulfones add anions readily and are dienophiles in the Diels–Alder reaction.[4] 1,3-Cycloadditions of diazo alkanes with acyclic[5a] and cyclic[5b] α,β-unsaturated sulfones are known. Adducts of diazo alkanes with thiete sulfone may be potentially useful intermediates in the synthesis of highly strained systems (such as bicyclobutanes) if the simultaneous or stepwise loss of both nitrogen and sulfur dioxide can be effected from the adducts. Cyclopropanes are formed by loss of nitrogen from 1-pyrazolines[6] and by loss of sulfur dioxide from certain four-membered cyclic sulfones (thietane sulfones).[7]

Addition of Diazo Alkanes to Thiete Sulfone.—Thiete sulfone yields crystalline adducts with various diazo alkanes. All of the adducts are 1-pyrazolines[8] with the exception of the adduct obtained from ethyl diazoacetate which forms a 2-pyrazoline. Table I lists the pyrazolines prepared. Where R and R′ are different groups, the stereochemistry (*syn,anti*) of the adducts was not determined although it is reasonable to assume

---

[1] This work was aided by Grant 5R01 CA 08250 of the National Institutes of Health, for which we are grateful.

[2] Reported at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstracts of Papers, Division of Organic Chemistry, No. 178.

[3] For further details, see R. Glassman, Ph.D. Thesis, Syracuse University, 1969.

[4] (a) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962); R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **28**, 2496 (1963); D. C. Dittmer and N. Takashina, *Tetrahedron Lett.*, 3809 (1964); R. Hasek, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **30**, 1495 (1965); L. A. Paquette and T. R. Phillips, *ibid.*, 3883 (1965); G. Opitz and H. Schempp, *Ann.*, **684**, 103 (1965); J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9**, 489 (1966); N. Takashina, unpublished observations. (b) D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **32**, 3872 (1967).

[5] (a) W. E. Parham, F. D. Blake, and D. R. Theissen, *ibid.*, **27**, 2415 (1962); L. I. Smith and H. R. Davis, Jr., *ibid.*, **15**, 824 (1950). (b) H. J. Backer, N. Dost, and J. Knotnerus, *Rec. Trav. Chim.*, **68**, 237 (1949).

[6] Reviewd by B. Eistert, M. Regitz, G. Heck, and H. Schwall, Houben-Weyl, "Methoden der Organischen Chemie, Stickstoffverbindungen I," Vol. X, part 4, G. Thieme Verlag, Stuttgart, 1968, p 810 ff, and by B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, New York, N. Y., 1967, p 118 ff.

[7] R. M. Dodson and G. Klose, *Chem. Ind.*, (London), 450 (1963); W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc* , **85**, 3236 (1963). Sulfur dioxide and a proton are lost readily from benzothiete sulfone giving possibly a benzocyclopropenium ion as indicated by mass spectrometry.[4b]

[8] Infrared absorption at 1540 cm^{-1} and ultraviolet absorption at 335 nm for –N═N–; no absorption for N—H in the infrared.

TABLE I

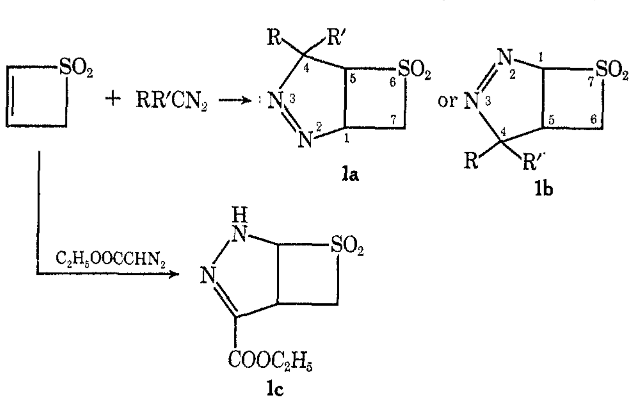
PYRAZOLINES DERIVED FROM THIETE SULFONE AND DIAZO ALKANES

R	R′	Structure
H	H	**1b**[a]
C_6H_5	H	**1a**
p-$CH_3OC_6H_4$′	H	**1a**
CH_3	H	**1a**
C_6H_5	D	**1a**
C_6H_5	C_6H_5	**1a**
C_6H_5	CH_3	**1a**
CH_3	CH_3	**1b**[a]
C_2H_5OCO	H	**1c**

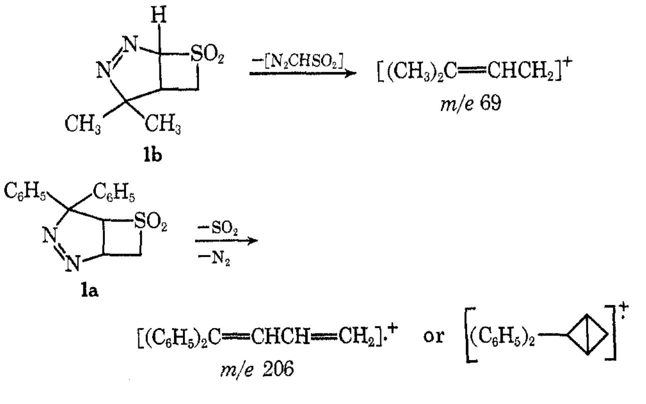
[a] Some **1a** also is formed.

that the more bulky group would prefer to be *anti* to the sulfone group.

Structure **1a** is favored for most of the adducts but a mixture of both **1a** and **1b** is formed from diazomethane and dimethyldiazomethane. The major adducts (**1b**) from the addition of diazomethane or dimethyldiazomethane show very intense peaks in their mass spectra corresponding to the loss of $[N_2CHSO_2]$. Adducts of structure **1a**, on the other hand, exhibit intense ions in their mass spectra corresponding to the loss of sulfur dioxide plus nitrogen. Since the plan for the synthesis of bicyclobutanes from the adducts calls for extrusion of sulfur dioxide and nitrogen from the 1-pyrazolines, the mass spectral data are promising. Scheme I illustrates the difference in fragmentation for adducts **1a** and **1b**.



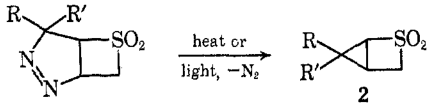
SCHEME I



The adduct **1b** of dimethyldiazomethane shows absorption at δ 7.18 (complex) in the nmr spectrum which is absent in adducts to which structure **1a** is assigned. This low field absorption is attributed to a proton situated on a carbon flanked by the azo group and the sulfone group and further supports structure **1b** for this particular adduct.

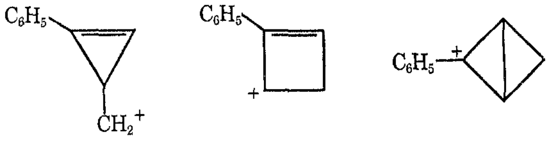
The initial adduct of ethyl diazoacetate presumably tautomerizes to the 2-pyrazoline (**1c**) because of the reactivity of the proton adjacent to the carbethoxy group in the 1-pyrazoline.

Loss of Nitrogen from Adducts.—When the pyrazoline obtained from thiete sulfone and diphenyldiazomethane or phenylmethyldiazomethane is heated at 130° or irradiated in the presence of benzophenone with light from a low pressure mercury lamp at room temperature,[9] nitrogen is lost to give the corresponding [2.1.0]thiabicyclopentane dioxide (**2**) in about 50% yield. These appear to be the first known thiabicyclopentane derivatives, but heterocyclic bicyclopentanes containing oxygen or nitrogen are known or have been proposed.[10]



R = R′ = C_6H_5–
R = C_6H_5; R′ = CH_3–

These thiabicyclopentane sulfones show absorption in the infrared at 1295–1300 and 1125–1150 cm^{-1} attributed to the sulfone group and at 1025–1028 and 855–867 cm^{-1} attributed to the cyclopropane ring.[11] The mass spectrum of the diphenyl derivative shows the formation of ions derived from the phenyl groups and ions attributed to $(C_6H_5)_2C^+$ and to the parent ion minus sulfur dioxide. The mass spectrum of the methyl phenyl derivative shows ions corresponding to a loss of sulfur dioxide and sulfur dioxide plus a methyl group from the parent ion. The abundant ions at *m/e* 129 may be cyclopropenylmethyl, cyclobutenonium, or bicyclobutane cations, or each may be some hybrid of the structures shown. The proton nmr spectrum of the diphenyl adduct is complex: absorption occurs at δ 7.30 (10 aromatic protons), 4.10 (complex multiplet $-CH_2SO_2-$), 3.55 (two doublets, cyclopropane proton nearest sulfone group), and 2.75 (triplet of doublets, other cyclopropane proton). In the methyl phenyl compound there is absorption at δ 7.34 (five phenyl protons), 4.10 ($-CH_2SO_2-$), 3.92 (cyclopropyl proton adjacent to $-SO_2-$), 2.60 (remaining cyclopropyl proton), and 1.74 (CH_3).



The diphenylthiabicyclopentane dioxide loses sulfur dioxide at high temperatures as well as in the mass spectrometer, but products have not been identified. Whether the thiabicyclopentane derivatives can be made to yield bicyclobutanes or whether they isomerize

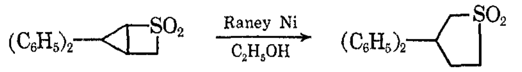
---

(9) Irradiation was done only with the diphenyldiazomethane adduct.

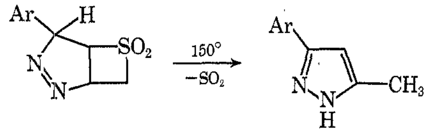
(10) C. D. Hurd and R. E. Christ, *J. Org. Chem.*, **1**, 142 (1936); G. A. R. Kon, L. F. Smith, and J. F. Thorpe, *J. Chem. Soc.*, **127**, 569 (1925); J. Bastus and J. Castells, *Proc. Chem. Soc.*, 216 (1962); M. Busch and J. Becker, *Ber.*, **29**, 1689 (1896); F. P. Woerner, H. Reimlinger, and D. R. Arnold, *Angew. Chem., Int. Ed. Engl.*, **7**, 130 (1968).

(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 2nd ed, 1958, p 29.

analogously to bicyclopentanes[12] remains to be determined. When the diphenylthiabicyclopentane dioxide was treated with Raney nickel, the cyclopropane ring was opened.



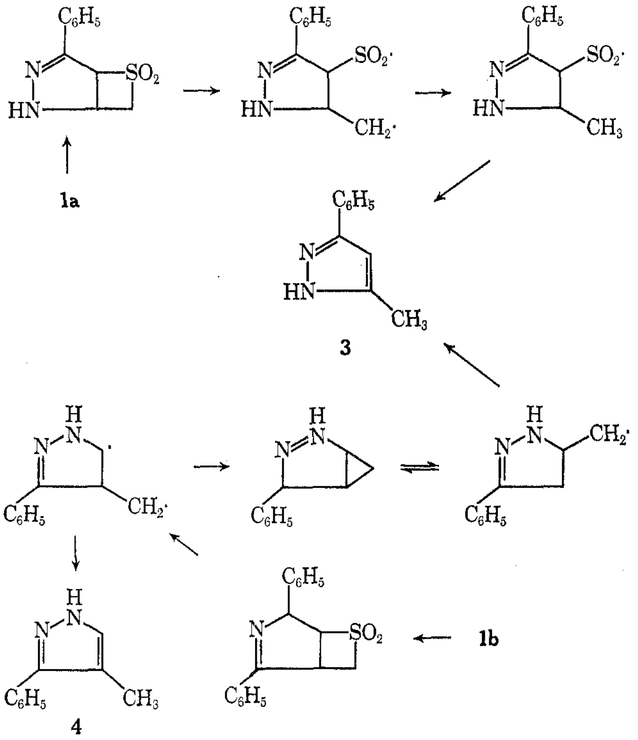
Loss of Sulfur Dioxide.—The adduct of thiete sulfone and phenyldiazomethane decomposes at 150° with loss of sulfur dioxide (but not nitrogen) to yield pyrazole **3** (52% Ar = C_6H_5), whose physical properties are identical with the physical properties of 3(5)-methyl-5(3)-phenylpyrazole which has been prepared previously from benzoylacetone and semicarbazide, hydrazine, or aminoguanidine.[13] If the adduct had structure **1b**, an isomeric pyrazole, 4-methyl-3(5)-phenylpyrazole (**4**), might have been formed (Scheme II), although isomerization of **1b** to **3** by way of a cyclopropane intermediate cannot be ruled out. None of **4** is observed. The adduct of thiete sulfone and *p*-methoxyphenyldiazomethane decomposes also to a pyrazole.



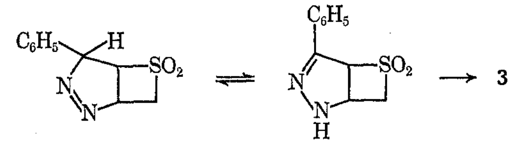
3

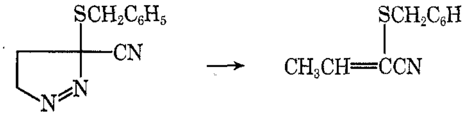
Ar = C_6H_5 or p-$CH_3OC_6H_4$–

SCHEME II



The formation of **3** from **1a** may proceed *via* a diradical as shown or *via* a zwitterion. Tautomerization to the 2-pyrazoline stabilizes the molecule to loss of nitrogen. The hydrogen transfer, which is shown from a diradical intermediate, is analogous to that observed in the loss of nitrogen from the 1-pyrazolines obtained from diazomethane and 1-benzylmercaptocrotonic acid nitrile or α-cyanoacrylic acids.[14]





Experimental Section[15]

Formation of 1-Pyrazolines. Addition of Diazomethane to Thiete Sulfone.—Thiete sulfone[16] (3.1 g, 0.030 mol) in 400 ml of ether was added to 150 ml of an ether solution of diazomethane,[17] prepared from Diazald (*p*-toluenesulfonylmethylnitrosamide, Aldrich, 21.5 g, 0.10 mol). The yellow solution was let stand at 0–5° for 4 days. Filtration gave 7-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 7,7-dioxide (3.2 g, 0.0219 mol, 73%), mp 105–112°. Three recrystallizations from chloroform produced an analytical sample, mp 113–114°.

Anal. Calcd for $C_4H_6N_2O_2S$: C, 32.88; H, 4.14; N, 19.17; S, 21.91. Found: C, 32.79; H, 4.18; H, 19.04; S, 21.87.

Ultraviolet spectrum ($CHCl_3$): 328 nm (ε 277). Infrared spectrum (KBr): 3000 (w), 2950 (w), 1540 (w), 1430 (m), 1410 (w), 1325 (s, doublet), 1290 (m), 1235 (m), 1220 (m), 1200 (m), 1180 (s), 1135 (s), 1100 (w), 1090 (m), 1035 (w), 980 (s), 940 (m), 915 (w), 890 (w), 845 (w), 820 (m), 770 (w), 745 (w) cm^{-1}. The 60-MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 7.16 (complex, 1 H, $N{=}NCHSO_2$), 4.85 (complex, 2 H), 4.40 (complex, 1 H), 3.85 (quartet, 1 H), 2.87 (complex, 1 H, H β to both N=N and SO_2). Mass spectrum:[18] *m/e* 28 (3.72), 29 (10.0), 39 (100), 40 (6.48), 41 (61.8), 42 (16.7), 43 (5.30), 44 (2.84), 45 (3.23), 48 (2.45), 52 (4.12), 53 (51.5), 54 (56.0), 55 (17.6), 61 (4.41), 62 (2.50), 63 (4.12), 64 (7.95), 69 (11.2), 70 (9.43), 71 (2.35), 72 (5.60), 73 (7.36), 76 (2.11), 82 (3.23), 146 (2.06).

Evaporation of the original filtrate produced more adduct (0.90 g, 0.00616 mol, 20.5%), mp 90°. Three recrystallizations from chloroform gave a mixture (mp 88–92°) of **1b** (R = R′ = H) and 6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (**1a**, R = R′ = H). The 60-MHz proton nmr spectrum of the mixture was taken in dimethyl sulfoxide-d_6 (all absorptions are complex): δ 7.16 (1.0 H, **1b**, $N{=}NCHSO_2$), 5.40 (1.6 H, **1a**, tertiary H α to N=N), 4.95 (6.7 H, **1a** + **1b**), 4.40 (2.8 H, **1a** +

---

[12] M. J. Jorgenson and T. J. Clark, *J. Amer. Chem. Soc.*, **90**, 2188 (1968), and references cited therein.

[13] (a) C. Runti and L. Sindellari, *Ann. Chim.* (Rome), **49**, 877 (1959); *Chem. Abstr.*, **54**, 4482 (1960). (b) G. N. Pershin, N. A. Novitskaya, A. N. Kost, and I. I. Grandberg, *Dokl. Akad. Nauk SSSR*, **123**, 200 (1958); *Chem. Abstr.*, **53**, 3490 (1959). (c) S. C. De and P. C. Rakshit, *J. Indian Chem. Soc.*, **13**, 509 (1936); *Chem. Abstr*, **31**, 1403 (1937).

[14] K.-D. Gundermann and R. Thomas, *Chem. Ber.*, **93**, 883 (1960); F. D. Popp and A. Catala, *J. Org. Chem.*, **26**, 2738 (1961); J. Hamelin, D. Vandevin, and R. Carrié, *Compt. Rend.*, **260**, 3102 (1965).

[15] Melting points are uncorrected and were obtained on a Fisher-Johns melting block. Infrared spectra were taken on a Perkin-Elmer Model 137 infrared spectrophotometer or on a Perkin-Elmer Model 521 grating spectrophotometer. The infrared absorptions are reported as weak (w), medium (m), strong (s); sh stands for shoulder. Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 ultraviolet spectrophotometer. The absorptions are reported in nanometers and the intensity (ε) of the absorptions in liter/mole-centimeter. Proton nuclear magnetic resonance (nmr) spectra were obtained on a Varian Model A-60 nmr spectrometer. Nmr absorptions are reported in parts per million (ppm) downfield from tetramethylsilane. Microanalyses were performed at Galbraith Laboratories, Knoxville, Tenn. Molecular weight determinations were done by vapor pressure osmometry in an appropriate solvent. Mass spectra were run at the Department of Chemistry, Syracuse University, Syracuse, N. Y., on a Perkin-Elmer Hitachi Model RMU-6E single-focusing spectrometer at an ionizing voltage of 20 V using direct inlet, unless otherwise noted. The internal ovens were kept at 250°, and each sample was heated at the lowest temperature which produced a spectrum.

[16] D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

[17] T. J. DeBoer and J. Backer, *Org. Syn.*, **36**, 16 (1956).

[18] Per cent of base peak is given in parentheses.

1b), 3.85 (1.5 H, **1a** + **1b**), 2.87 (1.0 H, **1b**, H β to both N=N and SO_2).

Addition of Phenyldiazomethane to Thiete Sulfone.—Thiete sulfone (1.0 g, 0.010 mol) in 200 ml of ether was added to 250 ml of an ether solution of phenyldiazomethane,[19] prepared from 10.0 g (0.045 mol) of azibenzil,[19] and the solution was allowed to stand at 0–5° for 1 day. A white solid was removed by filtration and recrystallized four times from chloroform to give 4-phenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (**1a**, R = C_6H_5; R′ = H) (1.2 g, 0.0055 mol, 55%), mp 161–162° dec.

Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.06; H, 4.54; N, 12.61; S, 14.40; mol wt, 222. Found: C, 53.89; H, 4.45; N, 12.59; S, 14.14; mol wt (chloroform), 245.

Ultraviolet spectrum: 331 nm (ϵ 315) (C_6H_6); 331 nm (ϵ 260) ($CHCl_3$). Infrared spectrum (KBr): 3000 (m), 2950 (w), 1540 (m), 1490 (m), 1450 (m), 1385 (m), 1340 (m, sh), 1310 (s), 1300 (m, sh), 1260 (m), 1250 (m), 1230 (m), 1190 (s), 1170 (s), 1120 (s), 1080 (m), 1070 (m), 1030 (w), 1020 (w), 1000 (w), 985 (w), 945 (w), 925 (w), 912 (w), 880 (w), 850 (m), 840 (w), 820 (w), 795 (w), 750 (m), 740 (s), 715 (m), 695 (s) cm^{-1}. The 60-MHz proton nmr spectrum was taken in dimethyl sulfoxide-d_6: δ 7.35 (complex, 5 H, C_6H_5), 6.47 (triplet, 1 H, $C_6H_5CHN{=}N-$), 5.85 (complex, 1 H), 5.00 (doublet, 1 H), 4.84 (quartet, 1 H), 4.39 (complex, 1 H). Mass spectrum:[18] *m/e* 55 (5.71), 83 (1.47), 91 (2.05), 102 (1.47), 103 (2.45), 104 (2.41), 115 (7.49), 116 (2.85), 127 (1.43), 128 (4.95), 129 (51.0), 130 (100) 131 (11.0), 158 (1.69), 194 (0.110).

Addition of *p*-Methoxyphenyldiazomethane to Thiete Sulfone.—A solution of *p*-methoxyphenyldiazomethane[20] in 100 ml of ether and thiete sulfone (1.0 g, 0.010 mol) in 250 ml of ether was let stand at 0–5° for 2 days. A solid was removed by filtration and recrystallized three times from methanol to produce an analytical sample of 4-*p*-methoxyphenyl-6-thia-2,3-diazabicyclo-[3.2.0]hept-2-ene 6,6-dioxide (**1a**, R = *p*-$CH_3OC_6H_4$; R′ = H) (1.5 g, 0.0060 mol, 60%) as white crystals, mp 131–133° dec.

Anal. Calcd for $C_{11}H_{12}N_2O_3S$: C, 52.38; H, 4.80; N, 11.11; S, 12.71; mol wt, 252.2. Found: C, 52.18; H, 4.68; N, 11.14; S, 12.65; mol wt (benzene), 268.

Ultraviolet spectrum: 328 nm (ϵ 348); ($CHCl_3$) 330 nm (ϵ 327) (CH_3SOCH_3). Infrared spectrum (KBr): 3030 (w), 2950 (w), 2870 (w), 1625 (m), 1600 (w), 1550 (w, sh) ,1525 (m), 1465 (w), 1450 (w), 1400 (w), 1340 (m), 1320 (s), 1295 (m, sh), 1255 (s), 1230 (m), 1200 (m), 1180 (s), 1140 (m), 1110 (m), 1075 (w), 1030 (m), 960 (w), 943 (w), 860 (m), 840 (m), 812 (m), 800 (w), 785 (w), 775 (m), 745 (m), 730 (w) cm^{-1}. The 60-MHz proton nmr spectrum was taken in dimethyl sulfoxide-d_6: δ 7.10 (complex, 4 H, C_6H_4), 6.45 (complex, 1 H, *p*-$CH_3OC_6H_4CHN{=}N$), 5.98 (complex, 1 H, H α to $-N{=}N-$), 4.85 (complex, 1 H, H α to $-SO_2-$), 4.35 (complex, 1 H, H α to $-SO_2-$), 3.77 (singlet, 3 H, *p*-$CH_3OC_6H_4-$), 3.32 (complex, 1 H, H α to $-SO_2-$). Mass spectrum:[18] *m/e* 45 (20.7), 55 (2.11), 64 (16.5), 115 (2.11), 117 (11.8), 128 (4.01), 129 (21.1), 130 (5.07), 131 (2.11), 132 (2.11), 144 (6.34), 145 (17.3), 146 (2.74), 147 (4.85), 158 (2.11), 159 (43.1), 160 (100), 161 (12.7), 175 (2.11), 188 (5.49), 224 (1.49).

Addition of Methyldiazomethane to Thiete Sulfone.—A solution of methyldiazomethane[21] in 250 ml of ether and thiete sulfone (3.1 g, 0.030 mol) in 400 ml of ether was let stand at 0–5° for 3 days. Filtration provided 4-methyl-6-thia-2,3-diazabicyclo-[3.2.0]hept-2-ene 6,6-dioxide (**1a**, R = CH_3; R′ = H) (3.2 g, 0.020 mol, 67%), mp 108–118°. Three recrystallizations from methanol produced an analytical sample of long white needles, mp 135°.

Anal. Calcd for $C_5H_8N_2O_2S$: C, 37.50; H, 5.04; N, 17.49; S, 19.99; mol wt, 160.1. Found: C, 37.54; H, 5.10; N, 17.61; S, 19.74; mol wt (acetone), 162.

Ultraviolet spectrum ($CHCl_3$): 323 nm (ϵ 233). Infrared spectrum (KBr): 2990 (m), 2950 (m), 1550 (w), 1480 (w, sh), 1450 (w), 1400 (m), 1380 (w), 1330 (s), 1310 (s), 1220 (m), 1200 (s), 1125 (s), 1105 (m, sh), 1090 (m), 1070 (m), 1025 (w), 990 (w), 940 (w), 915 (w), 860 (w), 830 (w), 785 (m), 765 (w, sh), 735 (m) cm^{-1}. The 60-MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 5.45 (complex, 2 H, CHN=NCH), 4.75 (complex, 2 H), 4.15 (2 quartets, 1 H), 1.28 [doublet (J = 8.0 cps), 3 H, CH_3]. Mass spectrum (70 V, indirect inlet):[18] *m/e* 50 (5.50), 51 (9.26), 52 (7.89), 53 (81.6), 54 (10.9), 55 (15.4), 56 (2.38), 57 (2.57), 61 (2.02), 62 (4.40), 63 (4.95), 64 (49.5), 65 (10.2), 66 (9.90), 67 (100), 68 (89.0), 69 (6.05), 81 (6.97), 95 (27.8), 96 (33.0), 97 (22.9).

Addition of Phenyldiazomethane-*α*-*d* to Thiete Sulfone.—A solution of thiete sulfone (1.0 g, 0.01 mol) in 400 ml of ether and phenyldiazomethane-α-d[22] in 125 ml of ether, prepared from 5.6 g (0.025 mol) of azibenzil,[19] was let stand at 0–5° for 2 days. Filtration and recrystallization from ether gave 4-deuterio-4-phenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (**1a**, R = C_6H_5; R′ = D) (1.2 g, 0.0054 mol, 54%) as a white solid, mp 136–138° dec. A second recrystallization from ether produced an analytical sample, mp 141–142° dec.

Anal. Calcd for $C_{10}H_9DN_2O_2S$: C, 53.90; H, 4.97; N, 12.58; S, 14.40; mol wt, 223.2. Found: C, 53.78; H, 4.88; N, 12.51; S, 14.56; mol wt (chloroform), 226.

Ultraviolet spectrum (C_6H_6): 329 nm (ϵ 300). Infrared spectrum (KBr): 3000 (w), 1540 (w), 1490 (w), 1450 (w), 1410 (w), 1400 (w), 1325 (s, doublet), 1250 (w), 1220 (m), 1210 (m), 1180 (s), 1140 (s), 1120 (m), 1100 (m), 1080 (w), 1050 (w), 1010 (w), 935 (w), 895 (w), 825 (w), 805 (w), 785 (w), 755 (m), 735 (m), 700 (m) cm^{-1}. The 60-MHz proton nmr was taken in dimethyl sulfoxide-d_6: δ 7.35 (complex, 5 H, C_6H_5), 5.85 (complex, 1 H), 4.91 (complex, 1 H), 4.55 (complex, 1 H), 4.25 (complex, 1 H). Mass spectrum (70 V, direct inlet):[18] *m/e* 74 (7.54), 75 (7.53), 76 (11.8), 77 (29.4), 78 (20.9), 79 (12.4), 81 (7.20), 89 (7.20), 90 (8.84), 91 (39.2), 92 (33.3), 102 (9.80), 103 (12.7), 104 (9.16), 105 (8.50), 115 (25.5), 116 (56.9), 117 (11.1), 118 (8.50), 124 (8.50), 127 (8.19), 128 (26.4), 129 (50.0), 130 (99.0), 131 (100), 132 (13.1), 157 (20.9), 158 (36.3), 159 (16.3), 195 (2.29).

Addition of Diphenyldiazomethane to Thiete Sulfone.—Diphenyldiazomethane[23] (3.9 g, 0.020 mol), prepared from benzophenone hydrazone (4.9 g, 0.025 mol), was added to thiete sulfone (1.0 g, 0.010 mol) in 400 ml of ether. The deep red solution was allowed to stand at 0–5° for 10 days. Evaporation of solvent produced a solid which was washed with cold ether and recrystallized twice from ether to give 4,4-diphenyl-6-thia-2,3-diazabicyclo-[3.2.0]hept-2-ene 6,6-dioxide (**1a**, R = R′ = C_6H_5) (1.5 g, 0.0050 mol, 50%), as long white needles, mp 151–152° dec.

Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.42; H, 4.73; N, 9.39; S, 10.73; mol wt 298. Found: C, 64.35; H, 4.51; N, 9.50; S, 10.84; mol wt (chloroform), 292.

Ultraviolet spectrum (95% C_2H_5OH): 341 nm (ϵ 310). Infrared spectrum (KBr): 3000 (w), 2930 (w), 1598 (w), 1540 (w), 1485 (m), 1440 (m), 1398 (w), 1320 (s), 1220 (s), 1200 (s), 1170 (s), 1130 (s), 1110 (m), 1090 (w), 1080 (w), 1050 (w), 1030 (w), 1000 (w), 990 (w), 980 (w), 930 (m), 920 (w), 900 (w), 892 (m), 840 (w), 760 (s), 745 (s), 690 (s) cm^{-1}. The 60-MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 7.50 (complex, 5 H, C_6H_5), 7.35 (complex, 5 H, C_6H_5), 4.18 (complex, 2 H), 3.25 (complex, 2 H). Mass spectrum:[18] *m/e* 64 (24.6), 74 (5.10), 91 (16.7), 115 (1.85), 128 (8.80), 129 (4.54), 165 (1.85), 191 (18.1), 192 (4.17), 204 (3.24), 205 (15.3), 206 (100), 207 (19.0), 208 (2.78).

Addition of 1-Phenyldiazoethane to Thiete Sulfone.—Thiete sulfone (2.1 g, 0.020 mol) in 400 ml of ether was added to 100 ml of an ether solution of 1-phenyldiazoethane,[24] prepared from acetophenone hydrazone[25] (15.0 g, 0.11 mol). The red solution was let stand at 0–5° for 1 day, and a white solid was removed by filtration. Two recrystallizations from methanol produced an analytical sample of 4-methyl-4-phenyl-6-thia-2,3-diazabicyclo-

---

(19) P Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958).

(20) *p*-Methoxyphenyldiazomethane was prepared from anisaldazine (10.0 g, 0.0373 mol, Aldrich) and anhydrous hydrazine (7.5 g, 0.23 mol, Matheson Coleman and Bell) according to the procedure of C. G. Overberger, N. Weinshenker, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **87**, 4123 (1967).

(21) Methyldiazomethane was prepared from N-ethyl-N′-nitro-N-nitrosoguanidine (16.1 g, 0.10 mol) and potassium hydroxide (22.4 g, 0.40 mol) according to the procedure of A. F. McKay, W. L. Ott, G. W. Taylor, M. N. Buchanan, and J. F. Crooker, *Can. J. Res.*, **28B**, 683 (1950); *Chem. Abstr.*, **45**, 4646 (1951).

(22) Phenyldiazomethane-α-d was prepared according to the same procedure for the preparation of phenyldiazomethane[19] by use of sodium deuteroxide (40% solution in D_2O) and methanol-d_6 (Diaprep, Inc., Atlanta, Ga.) in place of sodium hydroxide and methanol, respectively.

(23) Diphenyldiazomethane was prepared in (a) 6 hr according to the procedure of L. I. Smith and K. L. Howard, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 351, or (b) 75 min according to the procedure of J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

(24) H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).

(25) A. Schönberg, A. E. K. Fateen, and A. E. M. A. Sammour, *J. Amer. Chem. Soc.*, **79**, 6020 (1957).

[3.2.0]hept-2-ene 6,6-dioxide (1a, R = C_6H_5; R′ = CH_3) (3.9 g, 0.17 mol, 83%), mp 170° dec.

Anal. Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.93; H, 5.12; N, 11.86; S, 13.55; mol wt, 236. Found: C, 56.14; H, 5.13; N, 11.97; S, 13.81; mol wt (chloroform), 225.

Ultraviolet spectrum ($CHCl_3$): 251 nm (ε 350), 336 (190). Infrared spectrum (KBr): 3000 (w), 1540 (w), 1500 (w), 1465 (w), 1445 (w), 1410 (w), 1375 (w), 1325 (s, doublet), 1250 (w), 1225 (m), 1210 (m), 1190 (s), 1140 (s), 1125 (m), 1115 (m), 1100 (w), 1090 (m), 1070 (w), 1055 (w), 1040 (w), 1030 (w), 1005 (w), 950 (m), 930 (w), 920 (w), 905 (w), 865 (w), 810 (w), 797 (w), 764 (s), 741 (w), 695 (s) cm^{-1}. The 60-MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 7.45 (complex, 5 H, C_6H_5), 4.18 (complex, 1 H, N═NCH), 3.18 (complex, 3 H, $CHSO_2CH_2$), 1.50 (singlet, 3 H, CH_3–). Mass spectrum:[18] *m/e* 91 (4.94), 103 (0.988), 104 (1.11), 105 (5.68), 115 (2.10), 116 (2.06), 117 (3.46), 118 (1.07), 127 (2.35), 128 (8.40), 129 (100), 130 (14.0), 131 (35.0), 132 (5.18), 141 (1.69), 142 (3.21), 143 (17.3), 144 (51.8), 145 (8.89), 146 (1.15), 147 (0.823), 157 (3.34), 158 (0.989), 159 (2.47), 160 (1.98), 161 (2.84), 162 (1.81), 172 (0.949), 208 (2.18).

Addition of Dimethyldiazomethane to Thiete Sulfone.—Dimethyldiazomethane,[24] prepred from acetone hydrazone[26] (29 g, 0.4 mol) and yellow mercuric oxide (102 g, 0.47 mol) in 87 g of xylene (distilled), was added to thiete sulfone (1.0 g, 0.010 mol) in 300 ml of ether. The red color disappeared immediately and a white solid precipitated after a few minutes. The mixture was let stand at 0–5° for 7 days. Evaporation of solvent produced 4,4-dimethyl-7-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 7,7-dioxide (1b, R = R′ = CH_3) (1.05 g, 0.0060 mol, 60%). Three recrystallizations from ether produced an analytical sample, mp 199° dec.

Anal. Calcd for $C_6H_{10}N_2O_2S$: C, 41.38; H, 5.79; N, 16.09; S, 18.38; mol wt, 174.2. Found: C, 41.14; H, 5.79; N, 15.91; S, 18.43; mol wt (methanol), 184.

Ultraviolet spectrum (CH_3OH): 330 nm (ε 140). Infrared spectrum (KBr): 3000 (w), 2950 (w), 2880 (w), 1530 (w), 1470 (w), 1450 (w), 1405 (m), 1360 (m), 1330 (s), 1255 (w), 1220 (m), 1195 (s), 1150 (s), 1130 (s), 1055 (m), 1020 (w), 995 (w), 967 (w), 952 (w), 915 (m), 900 (w), 870 (w), 810 (w), 785 (m), 740 (w), 720 (w) cm^{-1}. The 60-MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 7.18 (complex, 1 H, N═NCHSO$_2$), 4.10 (comlex, 2 H, –SO_2CH_2), 2.68 (complex, 1 H, H β to –N═N– and –SO_2–), 1.55 (singlet, 3 H, CH_3–), 1.21 (singlet, 3 H, CH_3–), Mass spectrum:[18] *m/e* 41 (21.9), 42 (10.7), 43 (8.15), 53 (5.20), 67 (45.6), 68 (10.7), 69 (100), 70 (10.4), 76 (15.9), 81 (4.08), 82 (21.9), 83 (9.26), 95 (20.9), 97 (9.64), 100 (8.90), 110 (11.1).

Addition of Ethyl Diazoacetate to Thiete Sulfone.—A solution of thiete sulfone (0.52 g, 0.0050 mol) and ethyl diazoacetate[27] (1.7 g, 0.015 mol) was let stand in 30 ml of benzene (distilled) at room temperature for 4 days. Filtration and concentration of the filtrate yielded 4-ethoxycarbonyl-7-thia-2,3-diazabicyclo [3.2.0]hept-3-ene 7,7-dioxide (1c, 0.70 g, 0.0032 mol, 64%), mp 130–135°. Two recrystallizations from acetone produced an analytical sample, mp 149–151°.

Anal. Calcd for $C_7H_{10}N_2O_4S$: C, 38.54; H, 4.62; N, 12.84; S, 14.67; mol wt, 218.2. Found: C, 38.32; H, 4.75; N, 12.62; S, 14.36; mol wt (ethanol), 217.

Ultraviolet spectrum (95% C_2H_5OH): 229 nm (ε 5000). Infrared spectrum (KBr): 3220 (s), 2970 (m), 2900 (m), 2500 (w), 2380 (w), 1700 (s), 1480 (w), 1440 (m), 1390 (w), 1365 (m), 1290 (s), 1230 (w), 1180 (s), 1150 (m), 1100 (m), 1080 (s), 1060 (m), 1040 (s), 1010 (m), 945 (w), 885 (w), 875 (w), 845 (s), 805 (m), 795 (m), 750 (w) cm^{-1}. The 60-MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 8.95 (singlet, broad, 1 H, NH), 7.74 (singlet, 1 H, –NCHSO$_2$), 4.25 (quartet, 2 H, –OCH_2CH_3), 4.02 (broad, 3 H, SO_2CH_2 and N═CCH), 1.30 (triplet, 3 H, –OCH_2CH_3). Mass spectrum:[18] *m/e* 64 (71.8), 80 (10.1), 81 (17.6), 107 (41.5), 108 (26.4), 109 (35.2), 123 (14.5), 125 (100), 126 (15.7), 139 (20.8), 141 (16.4), 153 (28.9), 154 (47.2), 155 (12.0).

Thiabicyclopentanes. 5,5-Diphenyl-2-thiabicyclo[2.1.0]pentane 2,2-dioxide. Pyrolysis of 4,4-Diphenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-Dioxide.—4,4-Diphenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (1a, R = R′ = C_6H_5) (0.23 g, 0.00077 mol) was refluxed in 20 ml of commercial xylene (mixture of isomers, distilled) for 2.5 hr. Evaporation of xylene on a rotary evaporator left a brown solid, which was washed with cold ether and recrystallized from benzene–ether[28] to give 5,5-diphenyl-2-thiabicyclo[2.1.0]pentane 2,2-dioxide (2, R = R′ = C_6H_5) (0.10 g, 0.00039 mol, 50%) as white crystals, mp 198°.

Photolysis of 4,4-Diphenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-Dioxide.—A solution of 4,4-diphenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (1a, R = R′ = C_6H_5) 0.0745 g, 0.000250 mol) and benzophenone (0.0455 g, 0.000250 mol) in 250 ml of benzene (distilled from calcium hydride) was irradiated (low pressure mercury lamp) for 3 hr at room temperature. Evaporation of benzene left a white oil, which was recrystallized from ether, and then from benzene–ether to yield 5,5-diphenyl-2-thiabicyclo[2.1.0]pentane 2,2-dioxide (2, R = R′ = C_6H_5) (0.0300 g, 0.000111 mol, 45.0%), mp 198°.

When the thiabicyclopentane sulfone was heated at 260° (under nitrogen in a flask with a cold finger or in a sealed tube), a tar was formed. Sulfur dioxide was detected by odor and by an acidic reaction to wet pH test paper.

Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.10; H, 5.22; S, 11.84; mol wt, 270. Found: C, 71.25; H, 5.28; S, 11.69; mol wt (chloroform), 262.

Ultraviolet spectrum ($CHCl_3$): 268.5 nm (ε 380). Infrared spectrum (KBr, Perkin-Elmer 521): 3050 (w), 3010 (w), 2940 (w), 1600 (w), 1585 (w), 1495 (w), 1450 (m), 1405 (w), 1310 (s), 1265 (w), 1220 (s), 1165 (w), 1150 (s), 1105 (w), 1080 (w), 1035 (w), 1028 (w), 1000 (w), 956 (w), 934 (w), 912 (w), 867 (w), 846 (w), 817 (m), 775 (m), 760 (w), 750 (s), 740 (w), 705 (s), 690 (m) cm^{-1}. The 60-MHz proton nmr spectrum was run in deuteriochloroform: δ 7.40 (complex, 5 H, C_6H_5), 7.20 (singlet, 5 H, C_6H_5), 4.10 (complex, 2 H, –SO_2CH_2–), 3.55 (quartet, 1 H, cyclopropyl H α to –SO_2–), 2.75 (sextet, 1 H, cyclopropyl H β to –SO_2–). Mass spectrum (70 V, direct inlet): *m/e* 51 (23.1), 63 (12.8), 69 (25.6), 76 (12.8), 77 (23.1), 78 (15.4), 85 (64.1), 87 (28.2), 89 (15.4), 91 (61.5), 101 (43.6), 102 (15.4), 103 (25.6), 115 (20.5), 116 (15.4), 127 (18.0), 128 (35.9), 129 (25.6), 131 (33.3), 135 (28.2), 137 (12.8), 147 (18.0), 151 (28.2), 152 (12.8), 153 (18.0), 163 (15.4), 165 (28.2), 178 (20.5), 179 (12.8), 189 (15.4), 190 (15.4), 191 (33.3), 201 (18.0), 202 (18.0), 203 (28.2), 204 (25.6), 205 (53.9), 206 (100), 207 (20.5).

5-Methyl-5-phenyl-2-thiabicyclo[2.1.0]pentane 2,2-Dioxide.—4-Methyl-4-phenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (1a, R = C_6H_5; R′ = CH_3) (0.472 g, 0.002 mol) was heated in 20 ml of benzene (distilled) in a sealed tube at 150° for 3 hr. An ultraviolet spectrum of the benzene solution contained no absorption at 335 nm. Evaporation of benzene left a white oil, which was recrystallized from ether to give 5-methyl-5-phenyl-2-thiabicyclo[2.1.0]pentane 2,2-dioxide (2, R = C_6H_5; R′ = CH_3) (0.235 g, 0.00113 mol, 56.7%), mp 95–105°. A second recrystallization from ether produced an analytical sample, mp 110–111°. Alternatively, the pyrolysis was performed in refluxing xylene (distilled) overnight.

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.45; H, 5.81; S, 15.37; mol wt, 208.2. Found: C, 63.35; H, 5.59; S, 15.31; mol wt (benzene), 216.

Ultraviolet spectrum ($CHCl_3$): 253 nm (ε 167), 259 (210), and 265 (170). Infrared spectrum (KBr, Perkin-Elmer 521): 3070 (w), 3005 (w), 2990 (w), 2950 (w), 2920 (w), 1595 (w), 1575 (w), 1490 (m), 1435 (m), 1405 (w), 1375 (w), 1345 (w), 1335 (w), 1295 (s), 1265 (m), 1205 (s), 1155 (m), 1125 (s), 1105 (w), 1055 (w), 1025 (w), 1005 (w), 990 (w), 935 (w), 910 (w), 890 (w), 855 (w), 845 (w), 795 (w), 785 (w), 760 (s), 695 (s) cm^{-1}. The 60-MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 7.34 (singlet, 5 H, C_6H_5), 4.10 (complex, 2 H, $CHSO_2CH_2$), 3.92 (complex, 1 H, –$CHSO_2CH_2$–), 2.60 (complex, 1 H, cyclopropyl H β to –SO_2–), 1.74 (singlet, 3 H, CH_3). Mass spectrum:[18] *m/e* 64 (6.07), 76 (5.54), 78 (2.50), 91 (3.03), 102 (1.78), 103 (1.78), 104 (1.78), 105 (11.1), 115 (5.00), 116 (2.32), 117 (2.14), 127 (5.00) 128 (19.8), 129 (100), 130 (13.6), 131 (3.57), 141 (4.29), 142 (4.11), 143 (18.2), 144 (36.4), 145 (6.80), 208 (2.50).

Formation of Pyrazoles. Pyrolysis of 4-Phenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-Dioxide.—4-Phenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (1a, R = C_6H_5; R′ = H) (0.087 g, 0.00039 mol) was heated in a sublimator at 150° (3 mm) for 10 min. A white solid sublimed, mp 121–123°; three more sublimations produced an analytical sample of 3(5)-methyl-5(3)-phenylpyrazole (3, Ar = C_6H_5) (0.032 g,

---

(26) T. Curtius and L. Pflug, *J. Prakt. Chem.*, **44**, (2) 543 (1891).

(27) N. E. Searle, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 424.

(28) A solution was obtained by stirring the solid in refluxing ether and adding hot benzene dropwise until all the solid dissolved.

0.00020 mol, 52%), mp 124° (lit.[13] mp 128, 127, 125–126, and 127–128°). A picrate was obtained, mp 158° (lit.[29] mp 158°).

Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71; mol wt, 158.2. Found: C, 75.96; H, 6.22; N, 17.81; mol wt (benzene), 165.

Ultraviolet spectrum: 251 nm (ϵ 15,600) (CH_3OH); 248 nm (ϵ 9200) ($CHCl_3$). Infrared spectrum (KBr): 3170 (m), 3120 (m), 3075 (m), 3000 (m), 2920 (m), 2840 (m), 1595 (m), 1580 (m), 1520 (m), 1500 (m, doublet), 1465 (m), 1410 (w), 1380 (w), 1320 (m), 1295 (m), 1275 (m), 1205 (m), 1155 (w), 1130 (w), 1100 (w), 1080 (m), 1060 (w), 1030 (m), 1015 (w), 965 (m), 915 (w), 870 (m), 840 (w), 795 (w), 760 (s), 715 (m), 690 (s) cm^{-1}. The 60MHz proton nmr spectrum was run in deuteriochloroform and in carbon tetrachloride: δ 12.66 ($CDCl_3$), 13.50 (CCl_4) [singlet ($CDCl_3$), broad (CCl_4), 1 H, –NH–]; 7.43 ($CDCl_3$), 7.40 (CCl_4) (complex, 5 H, C_6H_5); 6.24 ($CDCl_3$), 6.15 (CCl_4) (singlet, 1 H, –C=CH–); 2.12 ($CDCl_3$), 2.15 (CCl_4) (singlet, 3 H, CH_3). Mass spectrum:[18] *m/e* 55 (1.37), 77 (0.99), 78 (0.76), 81 (0.76), 90 (1.52), 91 (0.46), 102 (0.38), 103 (1.75), 104 (0.91), 115 (0.91), 116 (0.61), 117 (2.81), 118 (0.61), 127 (0.38), 128 (1.37), 129 (1.60), 130 (2.81), 131 (0.53), 143 (2.05), 157 (16.4), 158 (100), 159 (11.6), 160 (0.76).

Pyrolysis of 4-*p*-Methoxyphenyl-6-thia-2,3-diazabicyclo[3.2.0]-hept-2-ene 6,6-Dioxide.—4-*p*-Methoxyphenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (**1a**, R = *p*-$CH_3OC_6H_4$–; R′ = H) (0.22 g, 0.00089 mol) was heated in a sublimator at 125° (5 mm) for 30 min. A white solid sublimed, mp 108°; two more sublimations produced an analytical sample of 3(5)-methyl-5-(3)-*p*-methoxyphenylpyrazole (**3**, Ar = *p*-$CH_3OC_6H_5$) 0.060 g, 0.00032 mol, 36%), mp 111°.

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.88; mol wt, 188.2. Found: C, 70.40; H, 6.62; N, 14.87; mol wt (chloroform), 206.

Ultraviolet spectrum ($CHCl_3$): 261 nm (ϵ 18,600). Infrared spectrum (KBr): 3100 (m), 3000 (m), 2850 (m), 1620 (w), 1580 (w), 1525 (m), 1460 (m), 1440 (m), 1300 (w, sh), 1275 (m), 1250 (s), 1210 (w, sh), 1180 (m), 1160 (m), 1115 (w), 1070 (w), 1025 (m), 1010 (m), 960 (w), 840 (m, sh), 830 (m), 810 (w), 790 (m, sh), 780 (m), 685 (w) cm^{-1}. The 60-MHz proton nmr spectrum was run in deuteriochloroform: δ 12.07 (singlet, 1 H, NH), 7.18 (quartet, 4 H, C_6H_4), 6.20 (singlet, 1 H, –C=CH), 3.76 (singlet, 3 H, CH_3O), 2.20 (singlet, 3 H, CH_3C=C). Mass spectrum (70 V, indirect inlet): *m/e* 90 (4.17), 91 (14.9), 92 (3.57), 94 (8.63), 102 (4.75), 103 (3.57), 104 (3.57), 115 (19.1), 116 (8.64), 117 (6.55), 145 (39.2), 146 (5.06), 159 (4.76), 173 (66.0), 174 (8.94), 188 (100), 189 (13.4).

5,5-Diphenyl-2-thiabicyclo[2.1.0]pentane 2,2-Dioxide. Reduction with Raney Nickel.—A solution of 5,5-diphenyl-2-thiabicyclo[2.1.0]pentane 2,2-dioxide (**2**, R = R′ = C_6H_5) (0.108 g, 0.00040 mol) in 40 ml of warm ethanol was added to a suspension of W-4 Raney nickel,[30] prepared from 10 g of nickel–aluminum alloy (K & K Laboratories, Jamaica, N. Y.) in 75 ml of 95% ethanol. The mixture was refluxed for 16 hr and the metal was removed by filtration from the hot solvent. Evaporation of ethanol left 3,3-diphenyltetrahydrothiophene 1,1-dioxide (0.052 g, 0.00019 mol, 47%) as a white solid, mp 135°. Two recrystallizations from ether produced an analytical sample of colorless crystals, mp 144–145°.

Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.58; H, 5.92; S, 11.75; mol wt, 272.3. Found: C, 70.78; H, 5.92; S, 11.69; mol wt (chloroform), 269.

Ultraviolet spectrum ($CHCl_3$): 253 nm (ϵ 208), 260 (238), 270 (ϵ 168). Infrared spectrum (KBr): 3010 (w), 2950 (w), 1600 (w), 1490 (m), 1450 (m), 1410 (w), 1400 (w), 1300 (s), 1240 (w), 1220 (s), 1180 (w), 1125 (s), 1090 (w), 1070 (w), 1030 (w), 1005 (w), 980 (w), 955 (w), 915 (w), 910 (w), 875 (w), 860 (w), 805 (w), 795 (w), 775 (m), 745 (s), and 700 (s), cm^{-1}. The 60 MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 7.35 [complex, 10 H, $(C_6H_5)_2C$–], 3.89 (complex, 4 H, $CH_2SO_2CH_2$), 3.05 (triplet, 2 H, –$CH_2CH_2SO_2$–). Mass spectrum (20 V, indirect inlet):[18] *m/e* 91 (9.10), 117 (8.44), 129 (16.7), 165 (10.4), 167 (48.9), 168 (6.75), 179 (8.60), 180 (100), 181 (15.8), 193 (42.1), 194 (6.85), 207 (25.2), 208 (6.24), 272 (9.70).

Registry No.—Thiete sulfone, 7285-32-7; 7-thia-2,3-diazobicyclo[3.2.0]hept-2-ene 7,7-dioxide, 23263-85-6; 3,3-diphenyltetrahydrothiophene 1,1-dioxide, 23263-97-0; **1a** (R = C_6H_5; R′ = H), 23263-86-7; **1a** (R = *p*-$CH_3OC_6H_4$; R′ = H), 23263-87-8; **1a** (R = CH_3; R′ = H), 23263-88-9; **1a** (R = C_6H_5; R′ = D), 23263-89-0; **1a** (R = R′ = C_6H_5), 23282-27-1; **1a** (R = C_6H_5; R′ = CH_3), 23263-90-3; **1b** (R = R′ = CH_3), 23263-91-4; **1c**, 23263-92-5; **2** (R = R′ = C_6H_5), 23263-93-6; **2** (R = C_6H_5; R′ = CH_3), 23263-94-7; **3** (Ar = C_6H_5), 3440-06-0; **3** (Ar = *p*-$CH_3OC_6H_4$), 23263-96-9.

---

(29) I. I. Grandberg and A. N. Kost, *Zh, Obshch. Khim.*, **28**, 3071 (1958); *Chem. Abstr.*, **53**, 10188 (1959).

(30) A. A. Pavlic and H. Adkins, *J. Amer. Chem. Soc.*, **68**, 1471 (1946).

The Thermal Decomposition of Benzenediazo Sulfones. I. Methyl Benzenediazo Sulfone[1]

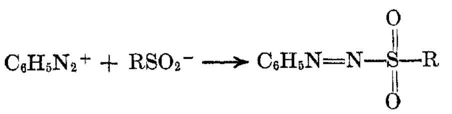
John L. Kice and Rolf S. Gabrielsen

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Received September 2, 1969

The thermal decomposition of methyl benzenediazo sulfone (**1c**) has been investigated in four different solvents. In three nonpolar solvents, benzene, cumene, and diphenylmethane, the principal identifiable decomposition products (Table I) are all ones that can be most easily interpreted as arising *via* a mechanism involving initial homolytic dissociation of **1c** and free-radical intermediates. The involvement of radical intermediates in the decomposition under these conditions is also shown by the results of experiments using a stable free radical (**2**) to scavenge the radicals formed by decomposition of **1c**. In the polar, aprotic solvent acetonitrile, on the other hand, the principal decomposition product, acetanilide, is thought to arise *via* an initial heterolytic dissociation of **1c** into a sulfinate and a benzenediazonium ion and reaction of the latter with the solvent in the manner shown in eq 10.

Benzenediazo sulfones (**1**) are an intriguing and little studied class of compounds which can be easily prepared by the reaction of a benzenediazonium salt with the salt of a sulfinic acid (eq 1). Although one reference work[2] claims that their thermal decomposition in nonpolar solvents leads to the formation of the sulfone $C_6H_5SO_2R$ and nitrogen, a study of the decomposition of phenyl



$$C_6H_5N_2^+ + RSO_2^- \longrightarrow C_6H_5N{=}N{-}\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}{-}R \qquad (1)$$

1

---

[1] This research was supported by National Science Foundation Grant GP-1975.

[2] Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 334.