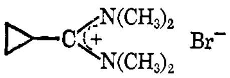
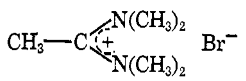
carboxamide: bp 75–78° (10 mm); n^{25}D 1.4673. The infrared and nmr spectra and the vpc retention time of the product were identical with those of an authentic sample prepared from cyclopropanecarboxylic acid chloride and dimethylamine. The initial products of the reaction, N,N,N′,N′-tetramethylcyclopropanecarboxamidinium bromide, **1**, and N,N,N′,N′-tetramethylacetamidinium bromide, **2**, could be observed by nmr spectroscopy in the unhydrolyzed reaction mixture but were not isolated.


1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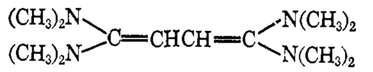
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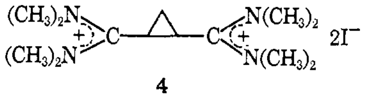
4

We also have found that 1,1,4,4-tetrakis(dimethylamino)-1,3-butadiene,[3] **3**, reacts smoothly with methylene iodide, 1:1 mole ratio, 24 hr at room temperature, acetonitrile solvent, to give 58% of *trans*-N,N,N′,N′,N″,N″,N‴,N‴-octamethyl-1,2-cyclopropanedicarboxamidinium diiodide, **4**: mp 252–254° dec; nmr (CF_3CO_2H) τ 6.60 (s, 24 $N(CH_3)_2$), 7.11 (m, 2, $^+CCH<$), 7.84 (m, 2, cyclopropane methylene). *Anal.* Calcd for $C_{13}H_{28}I_2N_4$: C, 31.59; H, 5.71; I, 51.36; N, 11.34. Found: C, 31.77; H, 5.83; I, 51.16; N, 11.35. Hydrolysis of the reaction mixture with dilute sodium hydroxide afforded 40% of *trans*-N,N,N′,N′-tetramethyl-1,2-cyclopropanedicarboxamide: bp 110–111° (0.3 mm); mp 57–60° [lit.[4] mp 56–58°]; nmr (CCl_4) τ 6.80 and 7.10 (singlets, 12 total, $-(O{=})CN(CH_3)_2$), 7.78 (m, 2, $-(O{=})CCH<$), 8.83 (m, 2, cyclopropane methylene). *Anal.* Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21; mol wt, 184. Found: C, 58.50; H, 8.69; N, 15.19; mol wt,[5] 184.

The scope of these cycloalkylation reactions of alkylidenebisdialkylamines and their application to the synthesis of other ring systems are being explored; the detailed results will be reported shortly.

[4] A. T. Blomquist and D. T. Longone, *J. Amer. Chem. Soc.*, 81, 2012 (1959).

[5] Mass spectroscopic determination.

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A Heterocycle with a Very Short (2.034 Å) S---O Intramolecular Distance

Sir:

Nitrosation of 2,5-diphenyl-6a-thiathiophthene and of 5-phenyl-1,2-dithiol-3-ylideneacetophenone yield a nitroso compound, $C_{17}H_{11}O_2NS_2$, for which structure I has been assigned on spectroscopic evidence.[1] Several examples of molecules with S—S---O groups involving carbonyl oxygen atoms have been examined by X ray crystallography,[2] but I offers an opportunity to study the influence of the nitroso group on such interactions; the crystal structure determination also serves to confirm that the nitroso group rather than the carbonyl group is in contact with S_3.

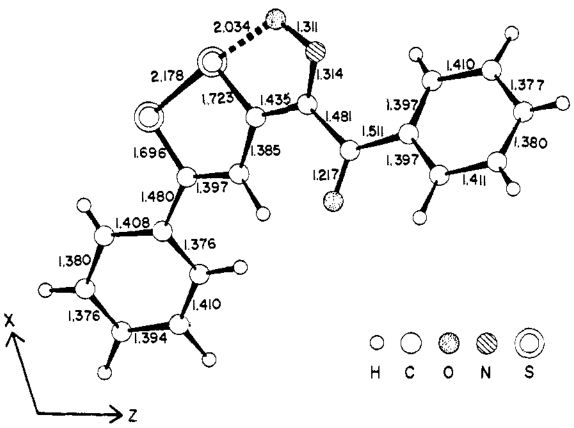
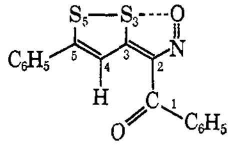


Figure 1. View of the molecule looking along the *b* axis. Bond distances in ångströms.


I

3,5-Epidithio-2-nitroso-1,5-diphenylpenta-2,4-dien-1-one (I) crystallizes as fine red needles (mp 172–173°) which belong to the monoclinic system;[3] *crystal data:* $C_{17}H_{11}O_2NS_2$, mol wt, 325.41; a = 15.545 (7), b = 4.065 (2), c = 24.297 (10) Å, β = 108° 13′ (3′); $V = 1535.3 \times 10^{-24}$ cm^3; ρ_{measd} = 1.39 g cm^{-3}; Z = 4, ρ_{calcd} = 1.408 g cm^{-3}; $F(000)$ = 672; absences, $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$; space group $P2_1/c$ (C_{2h}^5). Intensity data were collected by a θ–2θ scan from a crystal mounted on a Picker FACS-1 computer-controlled diffractometer (Cu Kα radiation). In all, 1777 reflections were judged to be above background. The structure was solved by the symbolic addition method[4] and has been refined by full-matrix least-squares methods, incorporating anisotropic temperature factors, to give a final R factor of 6.4% on the observed data. The molecular structure is shown in Figure 1.

The oxygen atom of the nitroso group is in very close contact with S_3 (2.034 (5) Å); this is 0.35 Å less than the shortest previously reported S---O intramolecular distance.[5] The S_3–S_5 distance (2.178 (2) Å) is similar to those found for the shorter S–S lengths in two un-

[1] R. J. S. Beer, D. Cartwright, R. J. Gait, R. A. W. Johnstone, and S. D. Ward, *Chem. Commun.*, 688 (1968).

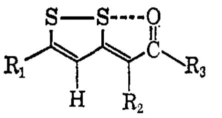
[2] M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, **192**, 1282 (1961); A. Hordvik, Abstracts, Summer Meeting of the American Crystallographic Association, Buffalo, N. Y., Aug 1968, Paper B1, p 32; A. Hordvik and H. M. Kjoge, *Acta Chem. Scand.*, **20**, 1923 (1966); A. Hordvik and E. Sletten, *ibid.*, **20**, 2043 (1966).

[3] The crystals were kindly supplied by Dr. R. J. S. Beer and Mr. R. J. Gait, University of Liverpool.

[4] J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

[5] For a compilation of such distances, see J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Am. Chem. Soc.*, **90**, 5800 (1968).

unsymmetrical thiathiophthene derivatives[6] but is significantly longer than the normal range of S–S covalent bond lengths (2.00–2.10 Å)[7] or than the S–S distances found in "dithiofurophthene" derivatives (IIa,b).[2]



IIa, $R_1 = CH_3; R_2 = H; R_3 = CH_3$
b, $R_1, R_2 = C_6H_5; R_3 = H$

The N–O length of 1.31 Å is somewhat longer than the values (1.14–1.24 Å) normally reported in nitroso compounds.[8] The C–N–O angle (113°) is much smaller than that found in *p*-iodonitrosobenzene (125°),[9] or even that for (+)-10-bromo-2-chloro-2-nitrosocamphane (118°),[10] while the C–N distance (1.31 Å) suggests substantial double bond character. The increase in length of S_3–C_3 over S_5–C_5, while not conclusively demonstrated by the analysis, is suggestive of additional bonding involving S_3.

The central eight atoms in I are significantly nonplanar (S_5, S_3, O, N, C_2, C_3, C_4, and C_5 lie 0.016, −0.018, 0.024, 0.054, 0.019, −0.016, −0.027, and −0.034 Å, respectively, from the best plane through the eight atoms); the greatest deviations from planarity occur in the dithiocyclopentene ring. The best planes through the two groups of five atoms (S_3, C_3, C_2, N, and O, and S_5, S_3, C_3, C_4, and C_5) are inclined at an angle of 2° 18′.

The molecular dimensions lead us to postulate significant bonding between S_3 and the oxygen atom of the nitroso group, certainly much more than is found in IIa or IIb. Recent MO calculations by Kapecki and Baldwin[11] imply virtually no covalent bonding between S and O in IIa. Klingsberg[12] has discussed examples where the S—S---O atoms are presumed to be in an approximate linear arrangement and for which various chemical and spectroscopic properties suggest d-orbital participation for the central sulfur atom.[13] Such participation may be an important factor in the bonding in I. The bonding in thiathiophthenes and in I may also be considered as an electron-rich three-center bond, as recently described by Gleiter and Hoffmann.[14] The S–S–O angle (174°) approaches the linear arrangement predicted to be most favorable to such a bond.[14,15]

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(6) A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, **20**, 2001 (1966); S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, and D. Cartwright, *Chem. Commun.*, 1170 (1967).

(7) A list of S–S covalent distances in various compounds is given by A. Hordvik, *Acta Chem. Scand.*, **20**, 1885 (1966).

(8) H. Ondik and D. Smith, "International Tables for X-ray Crystallography," Vol III, Kynoch Press, Birmingham, England, 1962, p 270.

(9) M. S. Webster, *J. Chem. Soc.*, 2841 (1956).

(10) G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *ibid.*, 1976 (1961).

(11) J. A. Kapecki and J. E. Baldwin, *J. Am. Chem. Soc.*, in press.

(12) E. Klingsberg, *J. Org. Chem.* **31**, 3489 (1966).

(13) For a pertinent review, see W. G. Salmond, *Quart. Rev.* (London), 22, 253 (1968).

(14) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968).

(15) Work supported by the National Institutes of Health (GM 12470-05) and the Hoffmann-La Roche Foundation.

(16) Alfred P. Sloan Foundation Fellow.

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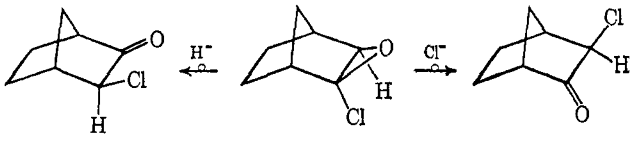
Molecular Rearrangements. VII.[1] Neat, Thermal Rearrangement of Optically Active 2-Chloronorbornene *exo*-Oxide

Sir:

Our product studies of neat, thermal rearrangements of 2-chloronorbornene *exo*-oxide (**1**) established that the two major products were *exo*-3-chloronorcamphor (**2**, ~37%) and *exo*-2-chloro-7-ketonorbornane (**3**, ~35%) and that **2** is not arising by isomerization of *endo*-3-chloronorcamphor, a minor (~4%) rearrangement product.[1] The formation of the major rearrangement product, **2**, can be rationalized by (1) chlorine as the migrating group, (2) an *endo*-3,2 hydride shift, or (3) multiple (*endo*-6,2, *exo*-5,6, and *endo*-3,5) hydride shifts.[2] Process 3 is equivalent to process 2 without suitable deuterium-labeling studies. Although most previous evidence discounts an *endo*-3,2 hydride shift, the recent observation of such a shift in the related pinacol rearrangement of *endo*-3-phenyl-*exo,cis*-2,3-bornanediol[3] strengthens this as a possibility.

We have now examined this neat, thermal rearrangement with optically active α-chloro epoxide **1** which allows a convenient way to determine if chloride (process 1) or hydride (process 2 or 3) migration occurs. If chloride migrates one enantiomer of **2**, **2a**, will be produced, while if hydride shifts occur the opposite enantiomer, **2b**, will be the product. The results show that >90% of the rearrangement proceeds by chloride migration.



2b **1** **2a**

The synthesis of optically active **1** began with *l*-α-pinene ($[\alpha]^{25}D$ −54.9° (*c* 2.0, ethanol)).[4] Hydroboration yields optically active diisopinocampheylborane which is allowed to asymmetrically hydroborate norbornene.[4] The product is (+)-(1*R*,2*R*)-*exo*-norborneol[5] ($[\alpha]^{27.5}D$ +2.78° (*c* 10.0, $CHCl_3$)) with an optical purity of about 95% based on the average value calculated by Berson and Suzuki.[6] Oxidation with Jones reagent yields (−)-(1*R*)-norcamphor[5] (**4**) ($[\alpha]^{27}D$ −18.18° (*c* 3.07, $CHCl_3$)) which, surprisingly to us, has

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(1) For paper VI in this series see R. N. McDonald and T. E. Tabor, *J. Org. Chem.*, **33**, 2934 (1968).

(2) For similar multiple hydride shifts in methylnorbornyl cations see J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2590 (1967), and previous papers in that series.

(3) A. W. Bushell and P. Wilder, *ibid.*, **89**, 5721 (1967).

(4) Obtained from Columbia Chemicals Co., Inc. This specific rotation is the largest yet reported for this compound; see H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964), and their ref 11.

(5) The absolute configurations of (−)-*exo*-norborneol and (+)-norcamphor have been assigned as 1*S*,2*S* and 1*S*, respectively, both by their relationship to terpenes of known absolute configuration (J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 1961)) and by ORD studies (K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962)).

(6) J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959), report $[\alpha]D$ +2.85–+3.02° for optically pure (+)-*exo*-norbornenol.