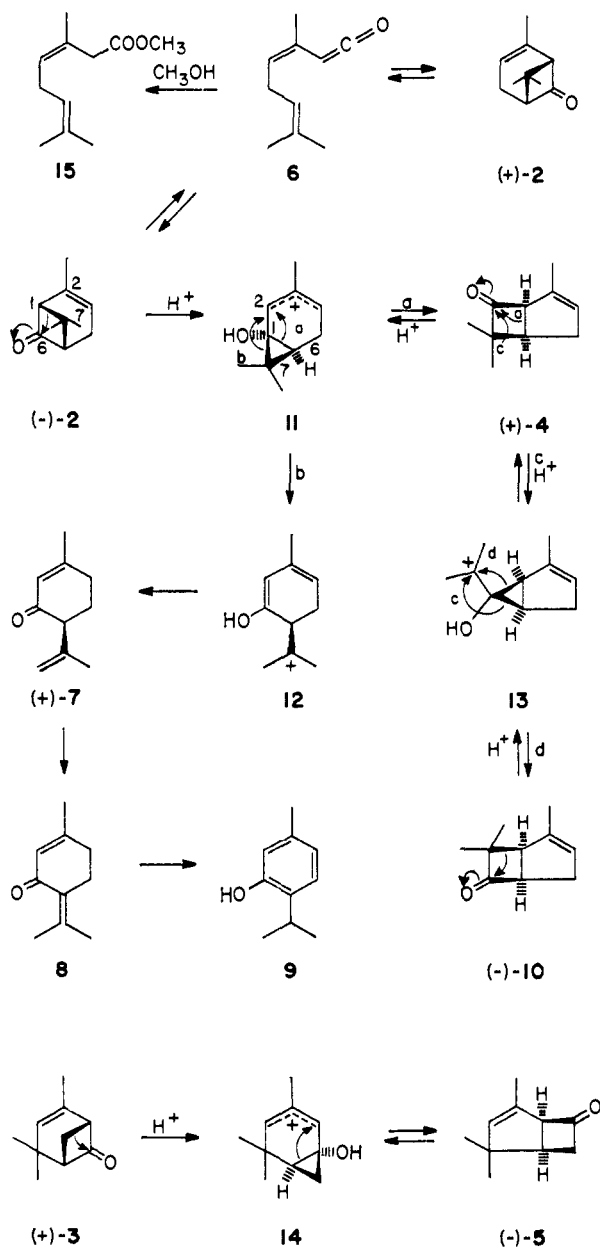


relative configuration of products, a mechanism for production of products is proposed which involves initial irreversible migration of the 1,7 bond in **2** to produce an intermediate cyclopropanol (**11**). Reversible migration of the 1,6 bond in **11** would afford **4** (path a), the product of kinetic control, while competitive scission of the 1,7 bond would produce **12**, the precursor of **7**, **8**, and **9** (path b). By the same type sequence of 1,2-alkyl shifts **10** would be produced from **4** via the intermediate **13** by a reversible process (paths c and d) and **5** from **3** via **14** (Chart I).

Chart I



Speculation about the mechanism by which racemized products are formed is obtained from the following observations. When **2** was heated at reflux (81°) under a nitrogen atmosphere in cyclohexane for periods of 16 and 77 hr, the recovered chrysanthenone (75–80% recovery) was 29 and 71% racemized, re-

spectively. Not even trace amounts of the ketone **4** were observed in the reaction mixture. Treatment of **2** with methanol at reflux (65°) for 16 hr produced *seq-cis*-1,7-dimethylocta-3,6-dienoate (**15**)¹ (37% yield) and 43% recovered **2**. The ketone **4** was recovered quantitatively with complete retention of configuration by similar treatment in cyclohexane and methanol. Pyrolysis of **2** ($[\alpha]^{25\text{D}} -36.6^\circ$) under a nitrogen atmosphere (or in an evacuated sealed tube) at 250° for 20 min afforded **4**, **7**, and **8** in yields of 16, 3, and 18%, respectively. The ketone **4**, though highly racemized, showed significant optical activity ($[\alpha]^{25\text{D}} +1.8^\circ$).

These observations indicate that **2** undergoes rapid interconversion with **6** even at temperatures as low as 65° at a much faster rate than thermal cyclization of **6** to **4**. Although **4** may be produced directly from **6** at higher temperatures (*i.e.*, 250° or greater), based on the above evidence, it is more probable that loss of retention in the production of **4** from **2** is the consequence of the rapid interconversion of **2** and **6**. Ketone **2** may then be converted to **4** by a slower, yet competitive, ionic process involving sequential 1,2-alkyl shifts.¹³ These proposals and other refinements of the mechanism are being considered in further detail and will be reported later.

Acknowledgments. We are grateful to Professor Ernest Wenkert for suggestions concerning the specific mechanisms described here and for making available to us information about his unpublished research on similar acid-catalyzed rearrangements of bicyclo[3.1.1]heptanones which support our findings here. The excellent technical assistance of Mr. Logan Stone is gratefully acknowledged.

(13) In our complete paper these observations will be used to explain the production of **4** from geranic acid,³ the racemization of **2** during glpc analysis^{4b} and fractional distillation,¹ and the production of products from pyrolysis of **4** at greater than 340° .³

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Received October 18, 1968

Cyclopropanes by Cycloalkylation of Alkylidenebisdialkylamines

Sir:

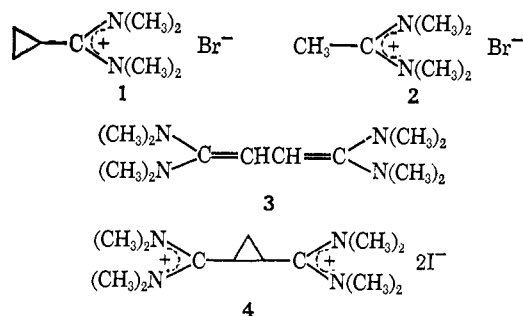
We wish to report the first examples of cycloalkylation of alkylidenebisdialkylamines to give cyclopropane derivatives. Whereas cycloalkylation of enamines of cyclic ketones with 1,4-diiodobutane and *o*-xylylene dibromide to give six-membered rings has been reported, no reaction was observed with 1,2-dibromoethane.¹ Enamines of aldehydes were reported to undergo N-alkylation, but not C-alkylation, with 1,2-dibromoethane.² In contrast, we have found that reaction of vinylidenebisdimethylamine³ with 1,2-dibromoethane, mole ratio 2:1, 24 hr at 70° , acetonitrile solvent, afforded, after hydrolysis with dilute sodium hydroxide, 34% of N,N-dimethylcyclopropane-

(1) G. Opitz and H. Mildenberger, *Ann.*, **650**, 115 (1961).

(2) G. Opitz and H. Mildenberger, *ibid.*, **649**, 26 (1961).

(3) H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 2874 (1966).

carboxamide: bp 75–78° (10 mm); n_D^{25} 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'*-tetra-



methylacetamidinium bromide, **2**, could be observed by nmr spectroscopy in the unhydrolyzed reaction mixture but were not isolated.

We also have found that 1,1,4,4-tetrakis(dimethylamino)-1,3-butadiene, **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 ($\text{CF}_3\text{CO}_2\text{H}$) τ 6.60 (s, 24 $\text{N}(\text{CH}_3)_2$), 7.11 (m, 2, $+\text{CCH}<$), 7.84 (m, 2, cyclopropane methylene). *Anal.* Calcd for $\text{C}_{13}\text{H}_{28}\text{I}_2\text{N}_4$: 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, $-(\text{O}=\text{C})\text{N}(\text{CH}_3)_2$), 7.78 (m, 2, $-(\text{O}=\text{C})\text{CCH}<$), 8.83 (m, 2, cyclopropane methylene). *Anal.* Calcd for $\text{C}_9\text{H}_{16}\text{N}_2\text{O}_2$: 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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Received November 21, 1968

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

Sir:

Nitrosation of 2,5-diphenyl-6a-thiathiophene and of 5-phenyl-1,2-dithiol-3-ylideneacetophenone yield a nitroso compound, $\text{C}_{17}\text{H}_{11}\text{O}_2\text{NS}_2$, for which structure **I** has been assigned on spectroscopic evidence.¹ Several

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

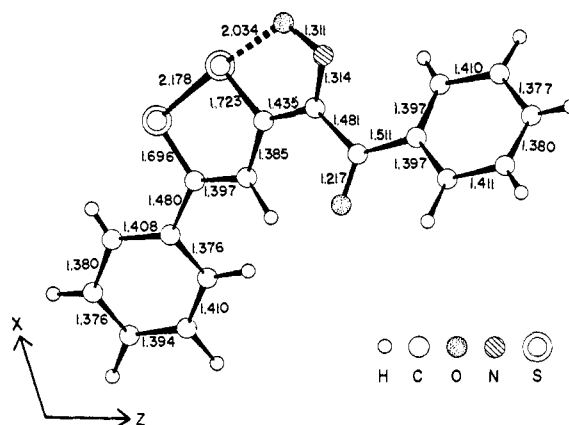
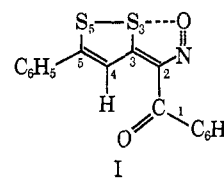


Figure 1. View of the molecule looking along the *b* axis. Bond distances in ångströms.

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 .



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*: $\text{C}_{17}\text{H}_{11}\text{O}_2\text{NS}_2$, mol wt, 325.41; $a = 15.545$ (7), $b = 4.065$ (2), $c = 24.297$ (10) Å, $\beta = 108^\circ 13'$ (3'); $V = 1535.3 \times 10^{-24}$ cm³; $\rho_{\text{meas}} = 1.39$ g cm⁻³; $Z = 4$, $\rho_{\text{calcd}} = 1.408$ g cm⁻³; $F(000) = 672$; absences, $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$; space group $\text{P2}_1/\text{c}$ (C_{2h}^2). Intensity data were collected by a θ - 2θ scan from a crystal mounted on a Picker FACS-1 computer-controlled diffractometer (Cu $\text{K}\alpha$ radiation). In all, 1777 reflections were judged to be above background. The structure was solved by the symbolic addition method⁴ 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-

(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. Kjøge, *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).