The mass spectrum indicated d_{16} (*m/e* 319) and a minor quantity of d_{15} (*m/e* 318). A sample of the hydrochloride was converted to the free base and purified by silica gel chromatography eluting with methanol–methylene chloride mixtures.

cis-B, **2-Piperidino-α-(*p*-methoxyphenyl)cyclohexanemethanol-d_{16}.**—A sample of *cis*-A free base was isomerized with trifluoroacetic acid as previously described.[1] The crude product was purified by silica gel chromatography and crystallization from ether (−20°), mp 133–135°. The mass spectrum was the same as the spectrum of the *cis*-A isomer.

Registry No.—*cis*-A, 13724-43-1; *cis*-B, 13724-46-4.

A Synthesis of Dihydrothiopyran-3-ones. The Intramolecular Cyclization of Allylthioglycolic Acid Chlorides

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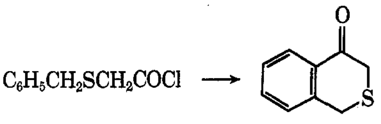
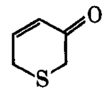
Intramolecular cyclization of allylthioglycolic acid chloride effected by aluminum chloride gave two products, 3,4-dihydro-2*H*-thiopyran-3-one and 3,6-dihydro-2*H*-thiopyran-3-one. Under similar conditions 3-methyl-, 2-methyl-, and 3,3-dimethylallylthioglycolic acid chloride produced 4-methyl- and 5-methyl-3,6-dihydro-2*H*-thiopyran-3-one and 4-isopropylidenetetrahydrothiophen-3-one, respectively. The substituent effects on the directionality of cyclization are discussed.

While the chemistry of thiopyrones have been widely investigated, little is known about the synthesis and chemical behavior of the isomeric thiopyran-3-one system. In the course of our study on the intramolecular cyclization of compounds containing heteroatoms, we are interested in thiopyran-3-ones, and we have now developed a novel and versatile synthesis for 3,6-dihydrothiopyran-3-ones bearing substituents on the ring.

The cyclization of benzylthioglycolic acid chloride reportedly produces isothiochromanone-4 (**1**).[1] Analogous formation of the parent thiopyranone **2** has not been reported.[2] We report here successful cyclization of allythioglycolic acid chlorides to the previously unknown thiopyranone.


$C_6H_5CH_2SCH_2COCl \rightarrow$

1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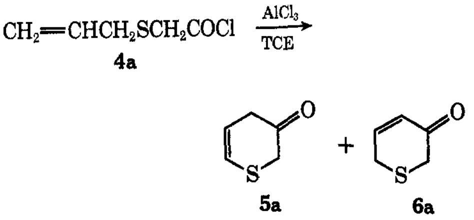
Allylthioglycolic acid (**3a**)[3] was synthesized in 82% yield by the reaction of allyl chloride with thioglycolic acid in aqueous sodium hydroxide solution. The acid was then converted into the acid chloride **4a** in 89% yield by the reaction with thionyl chloride. Treatment of acid chloride **4a** with aluminum chloride in 1,1,2,2-tetrachloroethane (TCE) at 50–55° gave **5a** and **6a** in a ratio of 53:47.

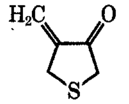

$CH_2{=}CHCH_2SCH_2COCl \xrightarrow[TCE]{AlCl_3}$

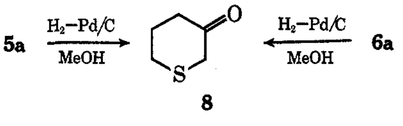
4a **5a** **6a**

The structure of the lower boiling compound **5a**, 3,4-dihydro-2*H*-thiopyran-3-one, was suggested by a combination of spectral data: ir 1710, 960, and 655 cm^{-1}; uv 221 and 242 mμ (α,β-unsaturated sulfide); nmr two methylene groups at δ 3.23 and 2.97 ppm, and two olefinic protons at δ 5.83 and 6.25 ppm (each double triplet).

Another higher boiling product **6a**, 3,6-dihydro-2*H*-thiopyran-3-one, was characterized by a carbonyl band at 1670 cm^{-1} and uv absorption maximum at 234 mμ, suggesting the presence of a CH=CHCO unit. The nmr spectrum of **6a** showed signals of two olefinic protons at δ 5.89 and 6.90 ppm (each double triplet), as well as two methylene groups at δ 3.20 and 3.21 ppm.

Cyclization of **4a** would be expected to lead to 3,6-dihydro-2*H*-thiopyran-3-one (**6a**), to 3,4-dihydro-2*H*-thiopyran-3-one (**5a**), or to 4-methylenetetrahydrothiophen-3-one (**7a**). The third possible product **7a** was not formed, since the ir spectra of products, especially that of the higher boiling material having a conjugated carbonyl function, showed no absorption of a methylene group at *ca.* 890 cm^{-1} or somewhat higher region,[4] and nmr pattern of olefinic proton signals of products is characteristic as a cis-disubstituted olefin rather than a exo methylene system (**7a**). The assignment of a thiopyran-3-one skeleton to our products was ultimately confirmed by catalytic reduction of **5a** and **6a** to the known ketone **8**.[5]


7a



8

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[1] (a) R. Lesser and A. Mehrländer, *Ber.*, *B*, **56**, 1642 (1932); (b) P. Cagniant and M. P. Cagniant, *Bull. Soc. Chim. Fr.*, 1998 (1959).

[2] Quite recently W. C. Lumma, Jr., and G. A. Berchtold [*J. Org. Chem.*, **34**, 1566 (1969)] have independently reported the synthesis and photochemistry of 5-methyl-3,6-dihydro-2*H*-thiopyran-3-one.

[3] (a) E. Larsson and B. O. Osberg, *Acta Chem. Scand.*, **14**, 768 (1960); (b) E. Larsson, *Ber.*, **63**, 1347 (1930).

[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 51.

[5] (a) N. J. Leonard and J. Figueras, Jr., *J. Amer. Chem. Soc.*, **74**, 917 (1952); (b) E. A. Fehnel, *ibid.*, **74**, 1569 (1952).

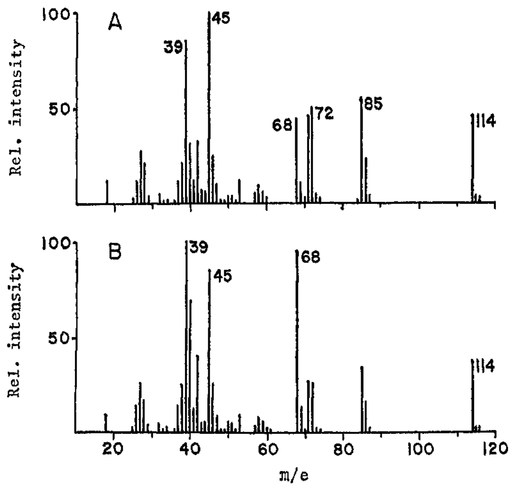
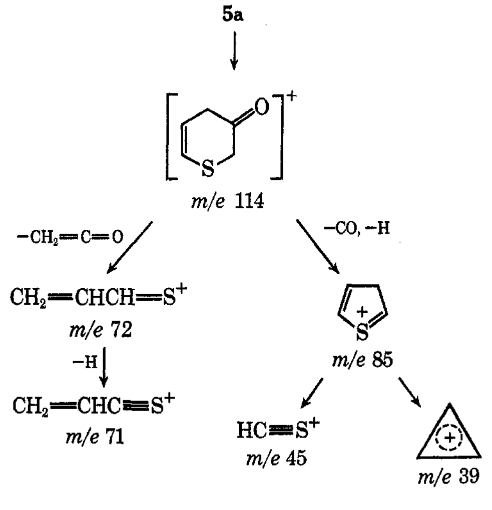


Figure 1.—Mass spectra of (A) **5a** and (B) **6a**.

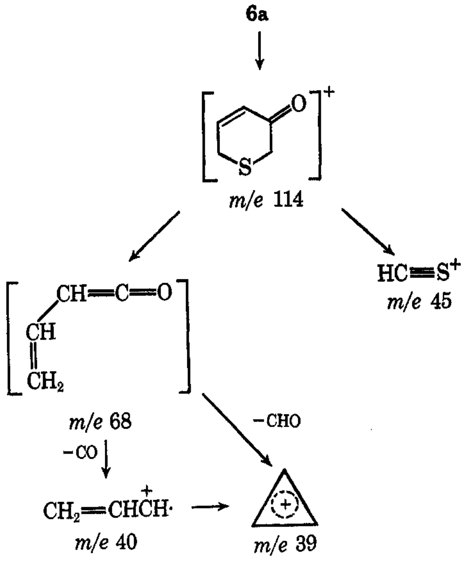
The position of the double bonds of **5a** and **6a** was additionally confirmed on the basis of mass spectral fragmentation pattern (Figure 1). Although both mass spectra of **5a** and **6a** indicate almost identical fragmentation, careful examination of relative intensity suggests that the structural assignment of $\Delta^{5,6}$-dihydrothiopyran-3-one and $\Delta^{4,5}$-dihydrothiopyran-3-one to **5a** and **6a**, respectively, is correct. Thus, the relatively intense peak of *m/e* 85 in the spectrum of **5a** compared to that of **6a** is caused by elimination of a molecule of CHO from the molecular ion to form a five-membered $C_4H_5S^+$ ion (85) which then degrades to the well-stabilized $HC{\equiv}S^+$ ion (45) and cyclopropenyl cation $C_3H_3^+$ (39). Two fragment ion peaks of *m/e* 72 ($C_3H_4S^+$) and 71 ($C_3H_3S^+$) seem to be produced by the elimination of ketene from **5a** by a retro-Diels-Alder fission (Scheme I).

SCHEME I
POSSIBLE FRAGMENTATION PATH OF **5a**



On the other hand, the main degradation path of **6a** is explained by bond fission between C-2 and C-3 and between C-6 and S, forming possibly vinylketene ion $C_4H_4O^+$ (68) and $HC{\equiv}S^+$. Further degradation of the former ion leads, with expulsion of CO, to allene ion (40) or, with lose of HCO, to the cyclopropenyl cation (Scheme II).

SCHEME II
POSSIBLE FRAGMENTATION PATH OF **6a**



Two strong peaks of $HC{\equiv}S^+$ (45) and $C_3H_3^+$ (39) which are frequently observed in the mass spectrum of sulfur-containing heterocyclic compounds,[6] may also be produced by a direct fission of **5a** and **6a**.

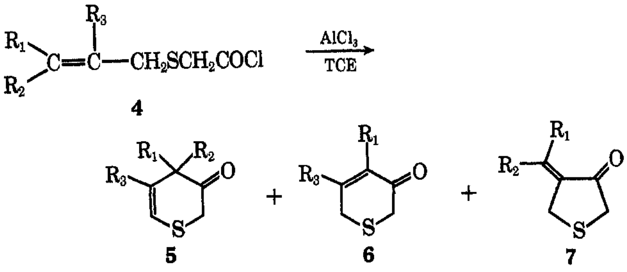
In order to examine the ratio of formation of **5a** and **6a**, a brief study of the influence of catalyst and solvent on the cyclization of **4a** was made, the results of which are summarized in Table I. In each case studied, 3,4-dihydro-2*H*-thiopyran-3-one was obtained in preferential amount.

TABLE I
CYCLIZATION OF **4a** IN VARIOUS CONDITIONS

Solvent	Catalyst	Temp, °C	Time, hr	Yield, %	Ratio, **5a**:**6a**
CS_2	$AlCl_3$	Reflux	4.5	23	65:35
TCE[a]	$AlCl_3$	50–55	4.0	42	53:47
TCE	$AlCl_3$	55–65	3.5	22	70:30
CS_2	$SnCl_4$	28–30	3.5	22	100:0
CS_2	$BF_3\cdot OEt_2$	Reflux	2.5	0	

[a] 1,1,2,2-Tetrachloroethane.

Cyclization of Substituted Allylthioglycolic Acid Chlorides.—The cyclization of allylthioglycolic acid chloride (**4a**) to give exclusively two isomeric six-membered cyclenones **5a** and **6a** without formation of any



a, $R_1 = H; R_2 = H; R_3 = H$
b, $R_1 = CH_3; R_2 = H; R_3 = H$
c, $R_1 = H; R_2 = H; R_3 = CH_3$
d, $R_1 = CH_3; R_2 = CH_3; R_3 = H$
e, $R_1 = C_6H_5; R_2 = H; R_3 = H$

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[6] G. Spiteller, *Advan. Heterocycl. Chem.*, **7**, 312 (1966).

five-membered-ring compound prompted us to examine the possible effect of alkyl substitution on the cyclization of the corresponding allylthioglycolic acid chloride. Thus, we have studied the cyclization of 3-methylallyl- (crotyl-), 2-methylallyl- (methallyl-), 3,3-dimethylallyl- (prenyl-), and 3-phenylallyl- (cinnamyl-) thioglycolic acid chlorides (**4b–e**). The acid chlorides **4b–d** were prepared from the corresponding acids **3b–d** with thionyl chloride, but the attempted synthesis of **4e** from cinnamylthioglycolic acid (**3e**) and thionyl chloride under various conditions was unsuccessful. Cyclization was carried out with aluminum chloride at 50–55° in TCE and results are summarized in Table II.

TABLE II

CYCLIZATION OF ALLYLTHIOGLYCOLIC ACID CHLORIDES

Compd	Temp, °C	Time, hr	Products	Yield, %
4a	50–55	4.5	**5a** (53%), **6a** (47%)	42
4b	50–53	2.5	**6b**	30
4c	50–53	2.5	**6c**	49
4d	50–53	1.5	**7d**	21

The structure assignment for the products emerged from an investigation of ir, uv, and nmr spectra.[7] As shown in Table II, the cyclization of **4b** or **4c** afforded single products, the six-membered, conjugated cyclenones **6b** and **6c**, respectively. However, **4d** was converted exclusively to the five-membered-ring ketone **7d**. This abnormal behavior is attributed to the stabilization of the carbonium ion from **4d** by methyl groups and/or the steric requirement of these methyl groups. Since the cyclization of 5-hexenoyl chloride has been reported to lead to 2-cyclohexenone and that of 5-heptenoyl chloride to 2-methyl-2-cyclohexenone,[9] substitution of C-3 methylene function of $\Delta^{5,6}$-unsaturated acid with thia linkage seems to exert no notable influence on the mode of the cyclization of acid chlorides.

Experimental Section

General.—Melting points and boiling points are uncorrected. The infrared spectra were recorded with a Hitachi Model EPI-S2 spectrophotometer and the uv spectra with a Hitachi Model EPS-3T spectrophotometer. The nmr spectra were obtained on a JEOL Model C-60H spectrometer in carbon tetrachloride solution with tetramethylsilane as an internal reference. The mass spectra were determined on a Hitachi Model RMU-6E spectrometer. Gas chromatography was carried out on a Shimadzu Model GC-1C gas chromatograph using a 3 mm × 260 cm column of 25% silicone DC200 on Celite 545 with He as the carrier gas.

Starting Materials.—3-Methylallyl alcohol,[10] 3-methylallyl bromide,[11] 3,3-dimethylallyl bromide,[12] and cinnamyl bromide[13] were prepared by the methods described in the literatures. The other chemicals were commercially available and purified by usual procedures before use.

Allylthioglycolic Acids (3a–e).—These acids were obtained by the modified procedure reported by Larsson and Osberg.[3a] 3-Methylallylthioglycolic acid (**3b**) was prepared in 65% yield: bp 94–98° (0.13 mm); $n^{20}{}_D$ 1.5057; ir 2930 (OH), 1705 (C=O), 960 cm^{-1} (CH=CH). *Anal.* Calcd for $C_6H_{10}O_2S$: C, 49.29; H, 6.89. Found: C, 48.81; H, 7.16.

Allylthioglycolic Acid Chlorides (4a–d).—Allylthioglycolic acid (**3a**) (16.6 g, 0.13 mol) and a large excess of thionyl chloride (30 ml) were refluxed for 1 hr. After removal of the remaining thionyl chloride under reduced pressure, the residual oil was distilled to give 16.8 g of allylthioglycolic acid chloride [**4a**, 89%, bp 63–65° (6 mm)]. Crotylthioglycolic acid chloride (**4b**), methallylthioglycolic acid chloride (**4c**), and prenylthioglycolic acid chloride (**4d**) were similarly prepared, carbon disulfide being used as solvent in the case of **4c** and **4d**. The results are summarized in Table III.

3,4-Dihydro-2*H*-thiopyran-3-one (5a) and 3,6-Dihydro-2*H*-thiopyran-3-one (6a).—A solution of **4a** (15.2 g, 0.10 mol) in dry TCE (40 ml) was slowly added over a period of 3.5 hr to a stirred solution of anhydrous aluminum chloride (15.0 g, 0.11 mol) in dry TCE (80 ml) at 50–55°. Stirring was continued for 1 hr at 50–55°, and then the mixture was cooled and poured into ice and diluted hydrochloric acid. The organic layer was separated and the aqueous layer extracted with ether (four 30-ml portions). The combined organic layer was washed with saturated sodium bicarbonate solution, then saturated sodium chloride solution, and dried (Na_2SO_4). After the evaporation of solvent *in vacuo*, distillation of the dark residue gave a light yellow oil (4.8 g, yield 42%), bp 70–80° (12 mm). Gas chromatographic analysis at 150° and 30 ml/min He flow showed two peaks with retention times 3.1 (53%) and 4.2 min (47%). The products were separated by preparative gas chromatography over silicone DC200. Redistillation of the former gave **5a** as a colorless oil: bp 64–68° (5 mm); $n^{20}{}_D$ 1.5571; ir 1710 (C=O), 1390, 1238, 960 (CH=CH), 750, 655 cm^{-1}; uv λ_{max} (95% EtOH) 221 mμ (ϵ 3540), 242 (3140), 374 (94); nmr δ 2.97 (m, 2 H), 3.23 (s, 2 H), 5.83 (double t, 1 H, J = 9 and 3.7 Hz), 6.25 ppm (double t, J = 9 and 1.2 Hz); mass spectrum m/e (rel intensity) 114 (46), 85 (55), 72 (49), 71 (46), 68 (44), 45 (100), 40 (31), 39 (85), 27 (27). The semicarbazone had mp 164–170° dec (nitromethane).

Anal. Calcd for $C_6H_9ON_3S$ (semicarbazone): C, 42.09; H, 5.30; N, 24.54. Found: C, 41.86; H, 5.40; N, 24.33.

On the other hand, the distillation of the latter gave **6a** as a colorless oil: bp 70–72° (4 mm); $n^{20}{}_D$ 1.5642; ir 1670 (C=O), 1400, 1380, 1250, 875, 750, 695 cm^{-1}; uv λ_{max} (95% EtOH) 234 mμ (ϵ 6750), 367 (26); nmr δ 3.20 (s, 2 H), 3.21 (m, 2 H), 5.89 (double t, 1 H, J = 10.5 and 1.5 Hz), 6.90 ppm (double t, 1 H, J = 10.5 and 4.05 Hz); mass spectrum m/e (rel intensity) 114 (37), 85 (33), 72 (25), 71 (27), 68 (97), 45 (85), 40 (69), 39 (100), 27 (25).

Tetrahydrothiopyran-3-one (8).—The dihydrothiopyran-3-one **5a** (0.5 g) was hydrogenated in methanol in the presence of 5% Pd/C (1.0 g) at room temperature. Evaporation of the solvent gave **8** (0.2 g) as a colorless liquid: ir 2924, 1710 (C=O), 1228, 760 cm^{-1} (CSC); nmr δ 2.38 (m, 2 H), 2.40 (broad s, 2 H), 2.73 (m, 2 H), 3.09 ppm (s, 2 H); mass spectrum m/e (rel intensity) 116 (100), 61 (33), 60 (96), 55 (33), 46 (71), 42 (71), 41 (33), 39 (41). The semicarbazone had mp 163–164° (aqueous EtOH) (lit. mp 166.5–167°,[5a] 165–166°[5b]).

Olefin **6a** was similarly hydrogenated to give **8** which was identical with that obtained from **5a** by comparison of ir and nmr spectra and the retention time of glpc.

Tetrahydrothiopyran-3-one 1,1-dioxide was obtained as a colorless solid on treatment of **8** with excess 30% hydrogen peroxide in glacial acetic acid–acetic anhydride. Recrystallization of the product from ethanol afforded colorless crystals melting at 147–148° (lit.[5b] mp 140–140.5°). Nmr spectrum in DMSO-d_6 showed multiplets at δ 2.05, 3.42, and 4.30 ppm.

Anal. Calcd for $C_5H_8O_3S$: C, 40.52; H, 5.44. Found: C, 40.67; H, 5.53.

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[7] Cyclization of **4b** would be expected to lead to 5-methyl-3,6-dihydro-2*H*-thiopyran-3-one (**6b**) and/or 4-ethylidenetetrahydrothiophen-3-one (**7b**), but the latter formula was eliminated chiefly because of the small coupling constant (1.5 Hz) between the olefinic proton and the methyl protons on the olefin carbon. The coupling constant between these protons of **7b** would fall in the range of 4–10 Hz.[8]

[8] (a) D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 183; (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Long Island City, N. Y., 1966, pp 710–745.

[9] (a) M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 2955 (1958); (b) M. O. Riose, *C. R. Acad. Sci.*, **248**, 2774 (1959).

[10] R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 1197 (1947).

[11] W. G. Young and J. F. Lane, *ibid.*, **59**, 2051 (1937).

[12] J. Tanaka, T. Katagiri, and S. Yamada, *J. Chem. Soc. Jap.*, **87**, 877 (1966).

[13] P. A. Briscoe, F. Challenger, and P. S. Duckworth, *J. Chem. Soc.*, 1755 (1956).

TABLE III

ALLYLTHIOGLYCOLIC ACID CHLORIDES[a]

Compd	Yield, %	Bp, °C (mm)	$n^{20}D$	Ir, cm^{-1} C═O	C═C	═CH	C—S
4a	89	63–65 (6)	1.5104	1790	1635	930	700
4b	82	88–95 (13)	1.5108	1790	1660	970	700
4c	70	82–87 (15)	1.5060	1790	1645	903	700
4d	71	94–97 (10)	1.4889	1795	1665	840	700

[a] Satisfactory analytical values (±0.3% for C and H) were reported for all compounds: Ed.

4-Methyl-3,6-dihydro-2*H*-thiopyran-3-one (6b).—Essentially the same procedure as described above for the cyclization of **4a** was employed. From 4.2 g of **4b** was obtained 1.0 g (30%) of **6b**: bp 99–103° (15 mm); $n^{20}D$ 1.5491; ir 1670 (C═O), 1080, 893 cm^{-1}; uv λ_{max} (95% EtOH) 245 mμ (ϵ 4810); nmr δ 1.78 (d, 3 H, J = 1.5 Hz), 3.18 (s, 2 H), 3.29 (m, 2 H), 6.70 ppm (m, 1 H). The semicarbazone had mp 187–190° dec (aqueous acetic acid).

Anal. Calcd for $C_7H_{11}ON_3S$ (semicarbazone): C, 45.39; H, 6.00; N, 22.69. Found: C, 45.43; H, 6.11; N, 22.79.

5-Methyl-3,6-dihydro-2*H*-thiopyran-3-one (6c).—The cyclization of **4c** was effected as described above: yield 49%; bp 85–95° (15 mm); $n^{20}D$ 1.5423 [lit.[2] bp 105–106° (6 mm); $n^{20}D$ 1.5579]; ir 1670 (C═O), 1273, 1023, 887 cm^{-1}; uv λ_{max} (95% EtOH) 242 mμ (ϵ 7850); nmr δ 2.00 (s, 3 H), 3.10 (s, 2 H), 3.15 (nearly s with fine splitting, 2 H), 5.78 ppm (double d, 1 H, J = 1.5 and 3.0 Hz). The semicarbazone had mp 149–152° dec (aqueous acetic acid).

Anal. Calcd for $C_7H_{11}ON_3S$ (semicarbazone): C, 45.39; H, 6.00; N, 22.69. Found: C, 45.21; H, 6.11; N, 22.53.

4-Isopropylidenetetrahydrothiophen-3-one (7d).—The acid chloride **4d** was similarly treated with aluminum chloride in TCE for 1.5 hr. The usual work-up afforded a ketonic product **7d**: yield 21%; bp 100–108° (13 mm); $n^{20}D$ 1.5520; ir 1690 (C═O), 1618, (C═C), 1270, 1200 cm^{-1}; uv λ_{max} (95% EtOH) 257 mμ (ϵ 8700); nmr δ 1.92 (s, 3 H), 2.21 (t, 3 H, J = 2 Hz), 3.26 (s, 2 H), 3.61 (t, 2 H, J = 2 Hz). The semicarbazone had mp 177–178° (AcOH).

Anal. Calcd for $C_8H_{13}ON_3S$ (semicarbazone): C, 48.22; H, 6.58. Found: C, 48.39; H, 6.68.

Registry No.—**3b**, 29431-24-1; **4a**, 29431-25-2; **4b**, 29520-65-8; **4c**, 29431-26-3; **4d**, 29431-27-4; **5a**, 29431-28-5; **5a** semicarbazone, 29431-29-6; **6a**, 29431-30-9; **6b**, 29431-31-0; **6b** semicarbazone, 29431-32-1; **6c**, 16994-29-9; **6c** semicarbazone, 29431-34-3; **7d**, 29520-66-9; **7d** semicarbazone, 29431-35-4; **8**, 19090-03-0; tetrahydrothiopyran-3-one 1,1-dioxide, 29431-37-6.

Acknowledgment.—The authors wish to express their gratitude to Mr. Mitsuo Sato for capable technical assistance in these experiments.

The Thermal Reorganization of Benzonorbornadiene

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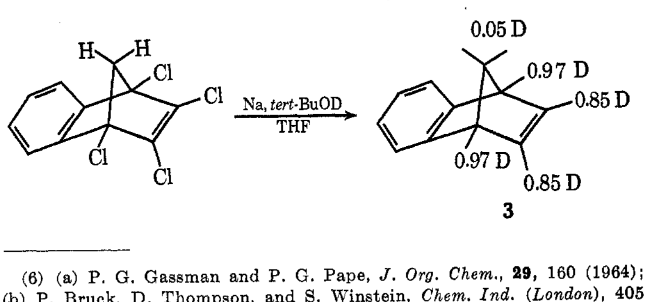
The thermal rearrangement of 2,3-benzonorbornadiene to 1,2-benzotropilidene has been shown, by deuterium labeling, to involve either benzonorcaradiene or 6,7-benzobicyclo[3.2.0]hepta-2,6-diene, or both. The norcaradiene valence tautomer of 1,2-benzotropilidene is ruled out as the first-formed intermediate.

Our interest in the thermal rearrangement of benzonorbornadiene (**1**) to 1,2-benzotropilidene (**2**) has led to a more detailed study of the mechanism of this reaction than previously reported.[3] We now wish to report on the thermal reorganization of the deuterium-labeled benzonorbornadiene (**3**) and its bearing on the mechanism of the reaction.

Treatment of hexachlorocyclopentadiene with zinc and glacial acetic acid afforded 1,2,3,4-tetrachlorocyclopentadiene[4] which, upon reaction with benzyne,[5] produced 1,4,5,6-tetrachloro-2,3-benzonorbornadiene, mp 92°, in 15% yield. The nmr spectrum (CCl_4) displayed an aromatic multiplet at τ 2.8 ppm and a singlet at τ 6.8 ppm, and the high-resolution mass spectral molecular weight confirmed the empirical formula. Treatment of the tetrachlorobenzonorbornadiene with sodium and *tert*-BuOD in THF, by a modification of the Winstein procedure,[6] afforded **3** in 82% yield. As needed, **3** was purified by preparative glpc. The deuterium content and distribution in **3** were determined by a com-



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[1] Author to whom correspondence concerning this work should be addressed at Yeshiva University. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

[2] National Science Foundation Undergraduate Research Participant, Summer, 1968, at Case Western Reserve University.

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