

TABLE III
 ALLYLTHIOGLYCOLIC ACID CHLORIDES^a

Compd	Yield, %	Bp, °C (mm)	<i>n</i> _D ²⁰	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 ($\pm 0.3\%$ for C and H) were reported for all compounds: Ed.

4-Methyl-3,6-dihydro-2H-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*_D²⁰ 1.5491; ir 1670 (C=O), 1080, 893 cm⁻¹; uv λ_{\max} (95% EtOH) 245 m μ (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 C₇H₁₁ON₃S (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-2H-thiopyran-3-one (6c).—The cyclization of **4c** was effected as described above: yield 49%; bp 85–95° (15 mm); *n*_D²⁰ 1.5423 [lit.² bp 105–106° (6 mm); *n*_D²⁰ 1.5579]; ir 1670 (C=O), 1273, 1023, 887 cm⁻¹; uv λ_{\max} (95% EtOH) 242 m μ (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 C₇H₁₁ON₃S (semicarbazone): C, 45.39; H, 6.00; N, 22.69. Found: C, 45.21; H, 6.11; N, 22.53.

4-Isopropylidene tetrahydrothiophen-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*_D²⁰ 1.5520; ir 1690 (C=O), 1618, (C=C), 1270, 1200 cm⁻¹; uv λ_{\max} (95% EtOH) 257 m μ (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 C₈H₁₃ON₃S (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

MARTIN POMERANTZ,*¹ THOMAS H. WITHERUP, AND WILLIAM C. SCHUMANN²

Departments of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and the Belfer Graduate School of Science, Yeshiva University, New York, New York 10033

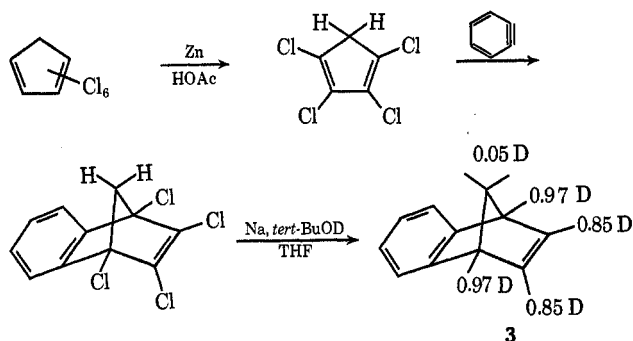
Received December 8, 1970

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-tetrachlorocyclopentadiene⁴ which, upon reaction with benzyne,⁵ produced 1,4,5,6-tetrachloro-2,3-benzonorbornadiene, mp 92°, in 15% yield. The nmr spectrum (CCl₄) 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-



(b) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); (b) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, **405** (1960). We wish to thank the late Professor Winstein for a copy of the procedure.

(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.

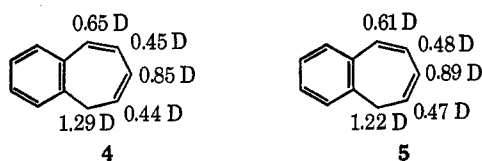
(3) M. Pomerantz and G. W. Gruber, *J. Org. Chem.*, **33**, 4501 (1968).

(4) E. R. Degginger and E. E. Gilbert, U. S. Patent 2,899,355; *Chem. Abstr.*, **53**, 22715a (1959).

(5) We are grateful to Professor Lester Friedman for the procedure for preparing the benzyne precursor, *o*-benzediazoniumcarboxylate hydrochloride; cf. R. M. Roberts, J. C. Gilbert, L. B. Rodewald, and A. S. Wingrove, "An Introduction to Modern Experimental Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1969, p 198.

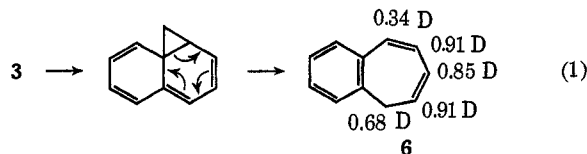
bination of low voltage mass spectroscopy (3.68 deuterons/molecule) and nmr spectroscopy.⁷

When **3** was heated at 345° for 15 min (gas phase, Pyrex ampoule), it was observed to have undergone *ca.* 15% conversion to the benzotropilidene **4**. This low conversion was necessary to ensure minimal scrambling of the 3, 4, 6, and 7 hydrogens in the 1,2-benzotropilidene, although, of course, 1,5-hydrogen shifts equilibrate the hydrogens α to the benzene ring along with those β to the benzene ring.⁸ Analysis of the deuterium content of **4** was by nmr spectroscopy.⁸



In a second run (340°, 66 min) the rearrangement proceeded to *ca.* 48% conversion and the deuterium labeling in the product was as indicated in **5**. Under these conditions the scrambling of positions 3 and 7 with 4 and 6 has already begun but has obviously not gone to equilibrium.³

If one considers the possible mechanisms which have not previously been eliminated,³ we can now discount the following one (eq 1) since this would require the



labeling indicated in **6**. This leaves two possibilities as originally postulated by Cristol and Caple,⁹ involving intermediates **7** or **8** (eq 2). In addition, if **8** was an intermediate it could give **7** (or its tropilidene valence tautomer). In either case; **7**, **8**, or valence tautomers could shift a hydrogen 1,5 (or 1,2; the overall result would be the same³) to produce **9** and finally **10** quite rapidly.³ Conversion to **11** would occur subsequently if the reaction is allowed to go to more than 10 or 20% completion.³ It is therefore seen that the observed deuterium distribution in **4** is, within experimental error, the same as predicted in eq 2.¹⁰ In addition, **5** is seen to be intermediate in deuterium distribution between **10** and **11**.

It should be pointed out that in one reaction run to *ca.* 50% completion both recovered starting material and the product displayed, within experimental error, the same deuterium distribution (d_0 , d_1 , d_2 , etc.) as the starting material as determined by mass spectroscopy.¹¹ Thus, no significant intermolecular scrambling occurs during the reaction.

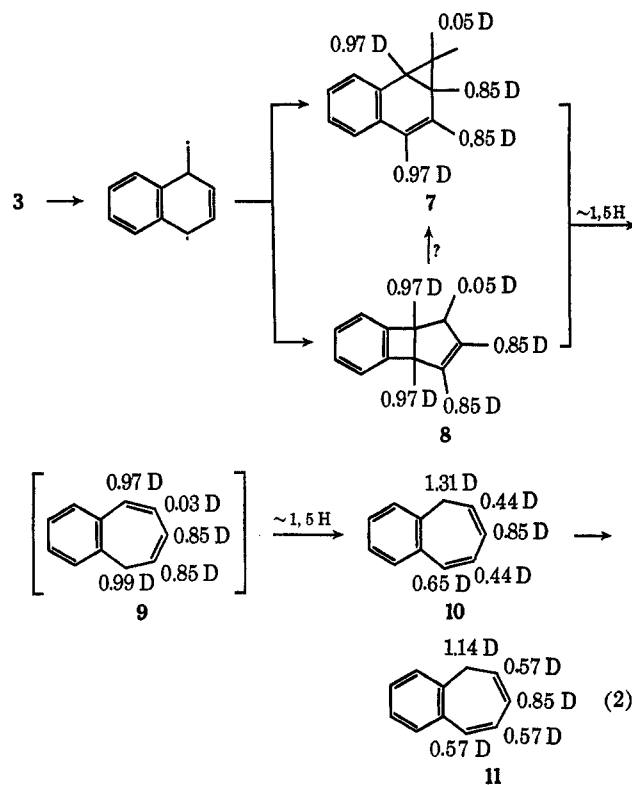
(7) The observation that there may be a trace of deuterium in the 7 position of **3** could be due to a trace of hexachlorocyclopentadiene in the tetrachlorocyclopentadiene which escaped glpc detection. The amount of deuterium is quite small, however, and might even be within experimental error of zero.

(8) In the case of **4** since we could not resolve the H_2 proton resonance from that of the aromatic protons, we assumed that H_2 contained half the amount of deuterium that was found in position 7.³

(9) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 585 (1966).

(10) If **10** had scrambled deuterium to the extent of *ca.* 10% (*i.e.*, 10% of **11**), this, too, would have been within the limits of experimental error.

(11) Unfortunately, for these determinations the voltage was slightly above the value which gives no fragmentation. Consequently a small P - 1 peak is present and thus the experimental error is larger than with the other mass spectra.



These experiments demonstrate the mechanism as shown in eq 2 involving either **7** or **8**, or both, as intermediates. In a large-scale pyrolysis using a flow system at 525° it was observed that the pot residue,¹² after distillation of the benzotropilidene through a Teflon spinning-band column, contained a trace amount of benzonorcaradiene. The material having the glpc retention time of benzonorcaradiene was collected. The nmr spectrum showed it to be mainly α - and β -methyl-naphthalene and 1,2-benzotropilidene, but the peaks in the spectrum above τ 7.7 ppm were superimposable with those of authentic benzonorcaradiene.¹³

Thus, while the observation of benzonorcaradiene in the pyrolysis of benzonorbadiene is consistent with the former being an intermediate on the way to 1,2-benzotropilidene, it does not itself prove the point. The present observations merely prove that one or both of the pathways depicted in eq 2 is the mechanism for the conversion of **1** to **2**.

Experimental Section

Mass spectra¹⁴ were obtained on a Varian M-66, a CEC 21-492, or an AEI MS 902 mass spectrometer and nmr spectra on a Varian A-60A spectrometer equipped with a C-1024 time averaging computer. Infrared spectra were from a Perkin-Elmer 257 or a Beckman IR-8 spectrometer. Gas chromatography columns were (1) 5 ft by 0.25 in. 20% SE-30 silicone rubber on 60-80 mesh Chromosorb W, (2) 12 ft by 0.25 in. 20% Carbowax 20M on 60-80 mesh Chromosorb P, and (3) 5 ft by 0.125 in. 5% SE-30 silicone rubber on 60-80 mesh Chromosorb W. The 0.25-in. columns were used with a thermal conductivity detector instrument while column 3 was used with a flame ionization detector instrument. Melting points are uncorrected.

1,2,3,4-Tetrachlorocyclopentadiene.—The procedure was basically that of Degginger and Gilbert,⁴ but with smaller quanti-

(12) We wish to thank Professor Lester Friedman and Mr. James C. Day, who ran this experiment, for a sample of their pot residue.

(13) We thank Dr. Gerald Gruber for this determination.

(14) We wish to thank Professor I. J. Borowitz of Yeshiva University, Mr. Harold Marsh of Case Western Reserve University, and Dr. Fred Abramson of CEC/Analytical Instruments Division for obtaining the mass spectra.

ties and longer time for the addition of zinc. In the first preparation, hexachlorocyclopentadiene (273 g, 1 mol) was mixed with 450 ml of glacial acetic acid in a 1-l. three-necked flask equipped with a thermometer, condenser, and stirrer. Zinc dust (150 g, 2.3 g-atoms) was gradually added to the rapidly stirred solution; the temperature of the very exothermic reaction was maintained below 75° with a Dry Ice-acetone bath. The addition required 55 min, after which the mixture was stirred for 35 min. The slurry which resulted was mixed with 1.5 l. of water. When the organic layer solidified it was filtered from the aqueous layer and dissolved in ligroin. This was filtered free of zinc particles, dried, and reduced in volume with a rotary evaporator to obtain light yellow crystals, mp 59–60° (lit.⁴ 61.6–62.4°), upon cooling. Glpc on column 3 at 100° showed the presence of a small amount of starting material.

In the second preparation, 136.5 g (0.5 mol) of hexachlorocyclopentadiene, 225 ml of glacial acetic acid, and 80 g (1.2 mol) of zinc dust were used. The addition time was 30 min, after which the mixture was stirred for 0.5 hr and treated the same as above.

The crystalline material, combined from both reactions, was sublimed under aspirator pressure to give a white solid (mp 61°) which showed no hexachlorocyclopentadiene by glpc (column 3 at 100°). The overall yield was 61.6 g (20% of theoretical); nmr (CCl₄) showed a singlet at τ 6.6 ppm.

***o*-Benzenediazoniumcarboxylate Hydrochloride.**—The procedure of Friedman⁵ was used in the preparation of this material. Into an 800-ml beaker surrounded by an ice bath was placed 27.4 g (0.2 mol) of anthranilic acid and 250 ml of absolute ethanol. The solution was stirred magnetically and when the temperature fell to 15° concentrated hydrochloric acid (23 ml) was added. Then isoamyl nitrite (55 ml) was slowly poured into the solution. This was stirred for 15 min, during which time light-colored granules began to appear. Absolute ether (250 ml) was added and the cold mixture was stirred for 30 min. The crystals were collected by suction filtration and washed with fresh absolute ether. The light pink solid was refrigerated until needed.

1,4,5,6-Tetrachloro-2,3-benzonornbornadiene.—The method of Friedman⁵ was used. In a typical reaction 9.3 g (0.05 mol) of *o*-benzenediazoniumcarboxylate hydrochloride and 11.3 g (0.055 mol) of tetrachlorocyclopentadiene were dissolved in 100 ml of ethylene dichloride contained in a 500-ml three-necked round-bottomed flask equipped with a thermometer, condenser connected to a bubble counter, mechanical stirrer, and heating mantle. Propylene oxide (4.4 g, 0.075 mol) was added and the medium was vigorously stirred while being slowly heated to reflux temperature. Gas evolution occurred and frothing was kept to a minimum by rapid stirring. After gas evolution ceased, most of the solvent was distilled and the resulting red-orange slurry was treated with petroleum ether (bp 30–60°).

The dark solution was filtered from the insoluble red-orange solid and the solvent was removed with a rotary evaporator. The resulting dark residue was steam distilled to obtain a light yellow solid which, when recrystallized several times from hexane, gave a white solid, mp 92°. The nmr spectrum displayed a multiplet centered at τ 2.8 ppm and a singlet at τ 6.8 ppm in the ratio of 2:1 (yield 4.6 g, ca. 15% of theoretical). Mass spectrum.¹⁴ Calcd for C₁₁H₆³⁵Cl₄: 277.9224. Obsd: 277.9222.

1,4,5,6-Tetradeuterio-2,3-benzonornbornadiene (3).—The Gassman^{6a} modification of the Winstein^{6b} procedure was employed in this reduction. A solution of 2.8 g (0.01 mol) of tetrachlorobenzonornbornadiene and 8.4 g (0.11 mol) of *tert*-butyl alcohol-*O*-*d* in 48 ml of dry tetrahydrofuran was prepared in a 100-ml, three-necked round-bottomed flask equipped with a nitrogen inlet, condenser connected to a bubble counter, thermometer, magnetic stirrer, and heating mantle. A dry nitrogen atmosphere was maintained, and sodium metal (6.0 g, 0.26 g-atom) was added in small quantities. The mixture was stirred and gradually heated to reflux. After 5 hr of refluxing, the mixture was stirred at room temperature for 2 days. The excess chunks of sodium were removed and methanol was added dropwise to the mixture. The resulting slurry was slowly poured onto 500 g of ice. The organic material was extracted with four 150-ml portions of ether, and the combined extracts were washed with three 200-ml portions of water and 200 ml of saturated sodium chloride solution. The ethereal solution was dried (anhydrous magnesium sulfate) and stripped of solvent; the brown-yellow oil was distilled under aspirator pressure to give a colorless liquid [bp 80–85° (55 mm), 1.1 ml, 1.3 g, 82% of theory]. Pure 1,4,5,6-tetradeuteriobenzonornbornadiene (3) was collected from glpc columns 1 or 2 operated at 195°. Low-voltage mass spectral analysis¹⁴ indicated 3.68 deuterons per molecule, and nmr analysis gave the distribution indicated (3).

Pyrolysis of 1,4,5,6-Tetradeuterio-2,3-benzonornbornadiene (3).—Compound 3 (150 μ l) was sealed under reduced pressure in a 50-ml base-washed Pyrex ampoule and heated for 1.1 hr at 340–343° (warm-up of 10 min from 308–340°). The product 5 and starting material were purified and analyzed by glpc (column 1 at 195°), which indicated about 47% reaction. Nmr analysis gave the deuterium distribution indicated in 5.

A second pyrolysis of 3 (150 μ l) at 342–345° for 15 min (warm-up of 10 min from 312–342°) followed by glpc analysis (column 2 at 195°) and purification indicated 15% conversion. The nmr spectrum of the product 4, in CCl₄, was obtained with the aid of a Varian C-1024 time averaging computer.¹⁵

Registry No.—Benzonornbornadiene, 4453-90-1.

(15) We wish to thank the National Science Foundation for a grant toward the purchase of the time-averaging computer.