# Notes

## Bridged Polycyclic Compounds. XXXIII. Thermal Rearrangement of Benzonorbornadiene[1]

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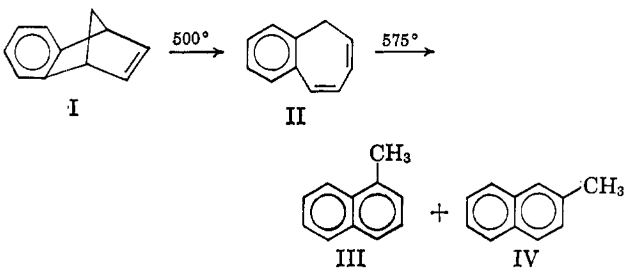
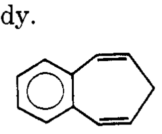
Pyrolysis of norbornadiene has been shown to lead to mixtures of cycloheptatriene (tropilidene) and toluene, and cycloheptatriene is converted to toluene under more severe conditions.[2-6] We have now observed that benzonorbornadiene (I) gives, at 500°, a mixture of 1,2-benzocycloheptatriene (II)[7] with small amounts of 1-methylnaphthalene (III) and 2-methylnaphthalene (IV). At higher temperatures, II is isomerized to III and IV.



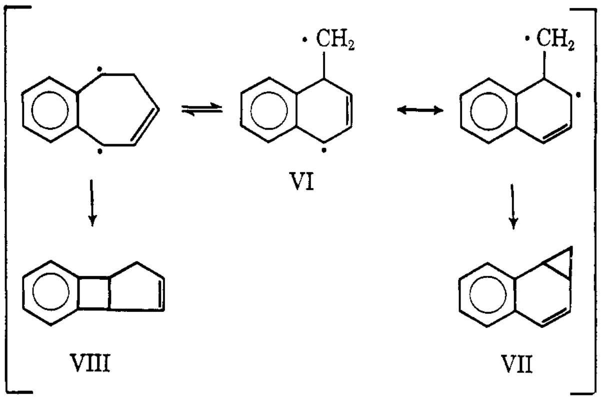
The structure of II[7] was confirmed by its p.m.r. spectrum. The methylene protons produce a sharp doublet at $\tau$ 7.10, $J = 6.2$ c.p.s. The four olefinic protons and four aromatic protons produce complex and unsymmetrical multiplets at $\tau$ 3.52–4.68 and 2.80–3.20, respectively. In tropilidene itself the methylene protons produce a triplet.[8] These data rule out the symmetrical 3,4-benzocycloheptatriene (V). In addition, the ultraviolet spectrum was identical with that reported for II and different from that reported for V. Wittig's[7] work indicates that the cross-conjugated triene V is unstable relative to II and the presence of V as a transient intermediate cannot be ruled out in the present pyrolysis study.



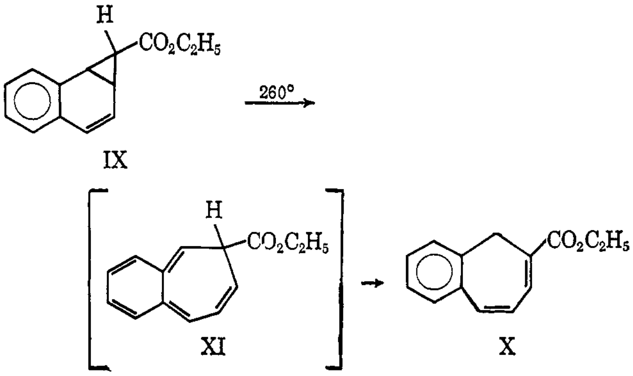
V

Although the rearrangement pathway is unknown, it can be rationalized as initially involving cleavage of the C-1–C-7 bond to form the diradical VI. The diradical VI may yield two plausible intermediates, benzonorcaradiene (VII) or 6,7-benzobicyclo[3.2.0]-hept-2-ene (VIII). However, neither these nor other intermediates could be isolated in the present product study, even when the pyrolysis temperature was dropped to *ca.* 425°, under conditions where the conversion of I to II was less than 25%.

In contrast to the formation of tropilidene from norbornadiene, the formation of II from I requires a hydrogen transfer in the rearrangement process. Intramolecular hydrogen shifts in diradical intermediates were first postulated in 1951 by Burwell[9] to account for certain reaction products resulting from the pyrolyses of the $\alpha$- and $\beta$-pinenes.



Consideration of VIII as a possible intermediate stems from the known rearrangement of bicyclo[3.2.0]-hepta-2,6-diene to tropilidene at 415°.[10] Benzonorcaradiene (VII) is considered a possible intermediate since an analogous thermal rearrangement has been noted by Huisgen and Juppe,[11] who observed that the ethoxycarbonylbenzonorcaradiene IX gives the 1,2-benzocycloheptatriene X. This also involves a hydrogen transfer. They suggest XI as a plausible intermediate, the hydrogen shift arising from the need to restore aromaticity. An analogous explanation appears plausible in the hydrocarbon series.



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[1] Paper XXXII: S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **31**, 581 (1966).

[2] W. G. Woods, *ibid.*, **23**, 110 (1958).

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[6] W. G. Herndon and L. L. Lowry, *ibid.*, **86**, 1922 (1964).

[7] G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

[8] For the spectrum of tropilidene, see N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1961.

[9] R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **73**, 4461 (1951).

[10] M. V. Evans and R. C. Lord, *ibid.*, **83**, 3409 (1961).

[11] R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961).

[12] A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

The mode of the subsequent rearrangement of II to the methylnaphthalenes III and IV, analogous to the rearrangement of tropilidene to toluene[2-6] and methyltropilidene to ethylbenzene,[12] is also uncertain. The formation of 1-methylnaphthalene (III), the major isomer, and 2-methylnaphthalene (IV) can be, however, most readily rationalized in terms of the benzonorcaradiene intermediate VII. The methylnaphthalenes were observed to be thermally stable at 575° and do not equilibrate.

## Experimental Section

**Pyrolysis of Benzonorbornadiene** (I).—The pyrolysis of freshly distilled benzonorbornadiene (I)[13] was accomplished by the dropwise addition, at a rate of about 5 ml./hr., of a 10% benzene solution of I onto a 0.25 × 12 in. Pyrex column filled with glass helices which was heated to the desired temperature. A slow stream of dry nitrogen was continuously passed through the column during pyrolysis. The pyrolysates were collected in a Dry Ice trap at the bottom of the column and the benzene was removed under vacuum. The material recovery was essentially quantitative and the product distribution was determined by v.p.c. and/or n.m.r. spectroscopy. At 500° the product ratio was 28% I, 68% II, 4% III, and only a trace of IV. The benzocycloheptatriene fraction II was separated by preparative v.p.c. and the ultraviolet spectrum was determined, $\lambda_{\max}^{\mathrm{CCl_4}}$ 278 m$\mu$ (log $\epsilon$ 3.8). The structures of the methylnaphthalenes were determined by v.p.c. and n.m.r. comparisons with authentic samples, the chemical shifts for the methyl signals of III and IV occurring at $\tau$ 7.57 and 7.72, respectively. With a column temperature of 575° the product distribution was 22% II, 66% III, and 12% IV. Column temperatures between 425 and 575° produced the expected transition in product ratios. The isomeric methylnaphthalenes III and IV were shown to be thermally stable at 575° and noninterconvertible at this temperature by passing authentic samples through the pyrolysis column.

**Analytical Methods.**—N.m.r. spectra were obtained in carbon tetrachloride with tetramethylsilane as the internal standard using a Varian Associates Model A-60 spectrometer. The gas chromatographic analyses were performed on a 2-m. silicone 710 column (30%) on Chromosorb, 35–80 mesh, at a column temperature of 164° and a helium flow rate of about 110 cc./min. The retention times for I, II, III, and IV were 7, 13, 14.5, and 13.5 min., respectively. For the preparative-scale separation of II, a 5-m. fluorosilicone, QF-1-0065, column (20%) on Anakron ABS, 70–80 mesh, at a column temperature of 185° and a helium flow rate of about 120 cc./min. was employed. The retention times for I, II, III, and IV on the fluorosilicone column were 24, 33, 46, and 37 min., respectively.

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# 2-Methyl-5,6-dihydro-1,4-dithiin and 2-Methyl-6,7-dihydro-5H-dithiepin from 2-Chloroallylthioalkanethiols[1]

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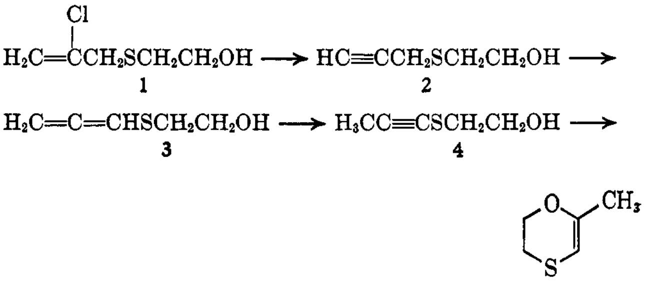
Treatment of 2-(2-chloroallylthio)ethanol (**1**) with base gives only one cyclic product, 2-methyl-1,4-oxathiene (**5**), which is formed by cyclization of 2-(1-propynylthio)ethanol (**4**).[2] In water, most of the **4** is formed from **1** by dehydrochlorination to 2-propargylthioethanol (**2**) followed by prototropic rearrangement of **2** to **4** *via* 2-allenylthioethanol (**3**). As allenylamines[3] and allenyl ethers[4] undergo intramolecular nucleophilic addition of alkoxide at the internal allenic carbon to give vinyl-substituted heterocycles, the fact that **1** gives no 2-vinyl-1,3-dithiolane indicates that prototropic rearrangement of an allenyl thio ether to a 1-propynyl thio ether occurs much more rapidly than addition of alkoxide to the internal allenic carbon.



$$H_2C{=}C(Cl)CH_2SCH_2CH_2OH \longrightarrow HC{\equiv}CCH_2SCH_2CH_2OH \longrightarrow$$

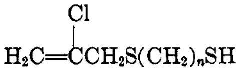
**1** **2**

$$H_2C{=}C{=}CHSCH_2CH_2OH \longrightarrow H_3CC{\equiv}CSCH_2CH_2OH \longrightarrow$$

**3** **4**

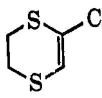
**5**

It appeared that substitution of more nucleophilic thiolate[5] for alkoxide in **1** would increase considerably the likelihood of bringing about an intramolecular nucleophilic addition to the internal allenic carbon. Consequently, we prepared the 2-chloroallylthioalkanethiols **6** and **7** and determined their mode of base-induced cyclization.

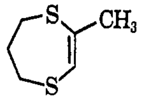


$$H_2C{=}C(Cl)CH_2S(CH_2)_nSH$$

**6**, $n = 2$
**7**, $n = 3$



**8**



**9**

The only cyclic product obtained from 2-(2-chloroallylthio)ethanethiol (**6**) on treatment with less than 1 equiv of potassium *t*-butoxide in *t*-butyl alcohol or, in poorer yield, with aqueous sodium hydroxide was 2-methyl-5,6-dihydro-1,4-dithiin (**8**). Similarly, 3-(2-chloroallylthio)propanethiol (**7**) gave 2-methyl-6,7-dihydro-5H-dithiepin (**9**) as the only cyclic product. Structural assignments to **8** and **9** were based on their infrared, ultraviolet, and nmr spectra, details of which are given in the Experimental Section.

Failure to observe any vinyl-substituted heterocyclic product from reactions of **6** and **7** with base indicates that nucleophilic addition to the internal allenic carbon of an allenyl thio ether capable of rearranging to a 1-propnyl thio ether is an extremely unlikely reaction.

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[1] Supported by Grant No. GM-10606 from the National Institute of General Medical Sciences of the U. S. Public Health Service.

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