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, $\lambda_{max}^{CCl_4}$ 278 mμ (log ε 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 τ 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.

Acknowledgments.—One of the authors (R. C.) is indebted to the National Science Foundation for aid in the form of a postdoctoral fellowship, 1964–1965. We are further indebted to the Institute of General Medical Sciences (Public Health Service Grant GM-12139) for partial support of this work.

(13) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

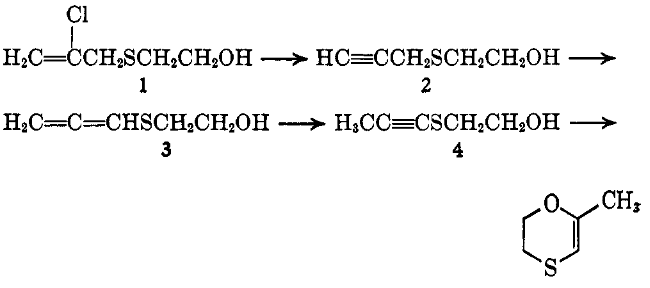
2-Methyl-5,6-dihydro-1,4-dithiin and 2-Methyl-6,7-dihydro-5H-dithiepin from 2-Chloroallylthioalkanethiols[1]

ALBERT T. BOTTINI AND ERNST F. BÖTTNER

Chemistry Department, University of California, Davis, California 95616

Received August 9, 1965

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.

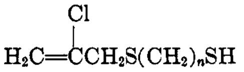


$$\underset{\mathbf{1}}{H_2C{=}\overset{Cl}{C}CH_2SCH_2CH_2OH} \longrightarrow \underset{\mathbf{2}}{HC{\equiv}CCH_2SCH_2CH_2OH} \longrightarrow$$

$$\underset{\mathbf{3}}{H_2C{=}C{=}CHSCH_2CH_2OH} \longrightarrow \underset{\mathbf{4}}{H_3CC{\equiv}CSCH_2CH_2OH} \longrightarrow$$

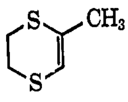
5

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.

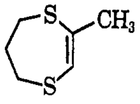


$$H_2C{=}\overset{Cl}{C}CH_2S(CH_2)_nSH$$

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.

---

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

(2) A. T. Bottini and E. F. Böttner, *J. Org. Chem.*, **31**, 385 (1966).

(3) A. T. Bottini, J. A. Mullikin, and C. J. Morris, *ibid.*, **29**, 373 (1964).

(4) A. T. Bottini, F. P. Corson, and E. F. Böttner, *ibid.*, **30**, 2988 (1965); A. T. Bottini and E. F. Böttner, *ibid.*, **31**, 389 (1966).

(5) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 7.

Experimental Section[6]

Compounds **6–9** *have particularly offensive odors.*

2-(2-Chloroallylthio)ethanethiol (**6**).—A solution was prepared from 375 ml of ethanol, 60 g (1.5 moles) of sodium hydroxide, and 141 g (1.5 moles) of ethanedithiol. The solution was stirred and cooled with an ice bath, and 111 g (1.0 mole) of 2,3-dichloropropene was added dropwise in 1 hr. Stirring was continued for 2 hr, and 90% of the ethanol was removed by distillation. The residue was allowed to cool, and 300 ml of water and 200 ml of ether were added. The phases were separated, and the aqueous phase was extracted twice with 100-ml portions of ether. The ether extracts were combined, washed with saturated sodium chloride solution, dried with magnesium sulfate, and distilled. Compound **6** (65 g, 38%) was collected at 85–100° (1 mm) and had $n^{24}\mathrm{D}$ 1.5645. The nmr spectrum consists of bands centered at 322 and 316 cps ($CH_2{=}$), a narrow band at 208 cps (${=}C{-}CH_2$), a multiplet from 157 to 180 cps (SCH_2CH_2S), and a triplet ($J \approx 8.1$ cps) at 97 cps (SH).

Anal. Calcd for $C_5H_9ClS_2$: Cl, 21.00. Found: Cl, 21.09.

When 1 mole of ethanedithiol instead of 1.5 moles was used, the yield of **6** was only 27 g (16%).

3-(2-Chloroallylthio)propanethiol (**7**) was prepared from 1,3-propanedithiol and 2,3-dichloropropene following a procedure similar to that used for **6**. The yield was 49 g (27%), bp 100–108° (0.5 mm), $n^{24}\mathrm{D}$ 1.5481. The nmr spectrum consists of bands centered at 324 and 318 cps (${=}CH_2$), a narrow band at 208 cps (${=}CCH_2$), a multiplet from 182 to 158 cps (SCH_2-CCH_2S), an apparent quartet ($J_{\mathrm{ap}} \approx 6.6$ cps) centered at 138 cps ($C{-}CH_2{-}C$), and a triplet ($J \approx 8.0$ cps) at 95 cps (SH).

Anal. Calcd for $C_6H_{11}ClS_2$: C, 39.44; H, 6.07; Cl, 19.40; S, 35.09. Found: C, 39.51; H, 5.94; Cl, 19.26; S, 34.88.

2-Methyl-5,6-dihydro-1,4-dithiin (**8**).—Of several procedures used, the following gave the best yield of **8**. To a stirred solution of 16.8 g (0.10 mole) of **6** and 20 ml of *t*-butyl alcohol at 75° was added dropwise in 2 hr a solution of 7.8 g (0.068 mole) of potassium *t*-butoxide and 60 ml of *t*-butyl alcohol. The reaction mixture was allowed to cool, and it was added to a mixture of 150 ml of water and 100 ml of ether. The phases were separated, and the aqueous solution was extracted twice with 70-ml portions of ether. The ether solutions were combined, dried with magnesium sulfate, and distilled to give 2.3 g (25%) of **8**, bp 73–74° (4 mm), $n^{22}\mathrm{D}$ 1.5972, $\lambda_{\max}$ 278 mμ (ϵ 3020), $\lambda_{\min}$ 256 mμ (ϵ 1380), λ 1600 cm^{-1} (C═C). The nmr spectrum consists of a quartet ($J \approx 1.5$ cps) at 318 cps (${=}CH$), a multiplet at 187–157 cps (SCH_2CH_2S), and a doublet ($J \approx 1.5$ cps) at 104 cps (CH_3).

Anal. Calcd for $C_5H_8S_2$: C, 45.41; H, 6.10; S, 48.49. Found: C, 45.33; H, 6.13; S, 48.66.

Before the preceding procedure was carried out, a similar reaction was run in which 11.2 g (0.10 mole) of potassium *t*-butoxide was used and the time for addition was 5 hr. During this run, gas–liquid partition chromatograms were taken to follow the course of the reaction. After 70% of the theoretical amount of potassium *t*-butoxide had been added, the intensity of the elution band due to **8** decreased relative to the height of the elution band due to *t*-butyl alcohol. The yield of **8** was 1.3 g (10%).

2-Methyl-6,7-dihydro-5H-dithiepin (**9**).—Treatment of 12.8 g (0.07 mole) of **7** with 7.8 g (0.07 mole) of potassium *t*-butoxide as described for the preparation of **8** gave 1.2 g (12%) of **9**, bp 73–75° (0.5 mm), $n^{26}\mathrm{D}$ 1.5881, $\lambda_{\max}$ 285 mμ (ϵ 4800), $\lambda_{\min}$ 255 mμ (ϵ 935), λ 1590 cm^{-1} (C═C). The nmr spectrum consists of a quartet ($J \approx 1.3$ cps) at 308 cps (${=}CH$), two apparent triplets, both with $J_{\mathrm{ap}} \approx 6.0$ cps, at 186 and 188 cps (CH_2-CCH_2), an apparent quintet ($J_{\mathrm{ap}} \approx 6.0$ cps) centered at 116 cps, and a doublet ($J \approx 1.4$ cps) at 101 cps (CH_3).

Anal. Calcd for $C_6H_{10}S_2$: C, 49.27; H, 6.89; S, 43.84. Found: C, 49.19; H, 6.82; S, 43.88.

---

(6) Boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-4 spectrophotometer. Nmr spectra were determined of compounds as 20% solutions in carbon tetrachloride at 56.4 Mc with a Varian Associates HR-60 system equipped with electronic integrator and base-line stabilizer. Resonance frequencies in nmr spectra were determined relative to internal tetramethylsilane (TMS) using the side-band technique with a Packard CD-200 audiooscillator and are reported in cycles per second downfield from the TMS resonance. Ultraviolet spectra were obtained of ethanol solutions using a Cary Model 14 recording spectrophotometer. Gas–liquid partition chromatograms were obtained using a Loe Model 1 Chromat-O-Flex with a 0.25 in. × 6 ft column packed with Silicone No. 550 on firebrick. Microanalyses were performed by Mr. V. H. Tashinian, Berkeley, Calif.

Conformational Analysis. VII. The Conformational Preference of the Nitro and Carboethoxyl Groups[1,2]

ROBERT J. OUELLETTE AND GARY E. BOOTH

Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210

Received September 14, 1965

In previous work[3] in which the relative stabilities of some carbomethoxyl and nitro bicyclic compounds were examined, it was assumed that the nitro and carbomethoxyl groups are sterically equivalent in systems which do not contain other substituents with nonbonded electrons. While the assumption appeared to be reasonable, there exists no definite experimental verification of the equivalence of the two groups.

Whereas the carboethoxyl and carbomethoxyl groups has been investigated by several techniques,[4] the nitro group has been little investigated save for its bond angles and bond lengths.[5] The necessary 4-*t*-butylnitrocyclohexanes are known, but base equilibration has not been carried out.[6] The nmr resonance signal for the α-hydrogen of the *cis* and *trans* isomers are τ 5.57 and 5.77, respectively. The corresponding resonance for nitrocyclohexane occurs at τ 5.72.[7] On the basis of agreement with a calculated spectrum it has been concluded that the nitro group is completely equatorial in nitrocyclohexane,[7] although the previous work of Huitric was apparently overlooked. While the experimental results of two groups of workers should not be used to calculate the conformational preference of the nitro group, it appears that nitrocyclohexane exists to a small extent in the axial conformation. Indeed, from the available experimental values the conformational preference of the nitro group is in the order of magnitude anticipated. Recently it has been reported that the agreement between calculated and experimental spectra for nitrocyclohexane is actually due to mathematical errors.[8] The details of the preliminary report will be outlined later.[9] Utilizing band widths, the calculated conformational equilibrium constant of 5.7 ± 1.5 at 26° is that anticipated for the nitro group.

We now report the determination of the conformational preference of the nitro group by direct equilibration. The nmr method is limited as the $-\Delta G$ for the nitro group is approximately 1.0 kcal/mole and the 12-cps difference between equatorial and

---

(1) Paper VI: R. J. Ouellette, K. Liptak, and G. E. Booth, *J. Org. Chem.*, **31**, 546 (1966).

(2) The authors acknowledge Grant No. 2410-A4 from The Petroleum Research Fund of The American Chemical Society in support of this research. A grant-in-aid from The Ohio State University is also acknowledged.

(3) R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **30**, 432 (1965).

(4) For references, see E. L. Eliel, N. L. Allinger, S. J. Argyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p 441.

(5) L. O. Brockway, J. Y. Beach, and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2693 (1935); E. Tannenbaum, R. J. Meyers, and W. D. Gwinn, *J. Chem. Phys.*, **25**, 42 (1956).

(6) A. C. Huitric and W. F. Trager, *J. Org. Chem.*, **27**, 1926 (1962).

(7) W. Hofman, L. Stefaniak, J. Urbanski, and W. W. Tanowski, *J. Am. Chem. Soc.*, **86**, 554 (1964).

(8) H. Feltkamp and N. C. Franklin, *ibid.*, **87**, 1616 (1965).

(9) Dr. H. Feltkamp, private communication.