

phenylthiazolines **1** and **7** on the basis of the observation that the molar extinction coefficients of *p*-nitrobenzamide derivatives and of *p*-nitrobenzoyl thiol esters (both potential hydrolysis products) were nearly identical in this spectral region. Thus, the optical density at completion of reaction would be nearly independent of the nature of the products (N-acyl- or S-acylcysteamines) and unaffected by possible S → N acyl transfer at the higher pH values. With the *m*-nitrophenylthiazoline **2**, it was noted that the rapidly reached final optical densities below pH 1 were significantly higher than the slowly attained final values above pH 2. It was assumed that the hydrolysis product in strongly acidic solution was mainly the S-acylcysteamine, which rearranged rapidly above pH 2 to the N-acylcysteamine of lesser extinction. In the pH range 1–2, "final" optical densities drifted slowly downwards, presumably as a result of slow rearrangement, and rate constants for hydrolysis were not evaluated in this pH region.

In all cases, initial thiazoline concentration was chosen so as to give an initial optical density of 1.2 (concentrations varied from 5×10^{-5} to 5×10^{-4} M). The pseudo-first-order rate constants were calculated using the expression

$$k = \frac{2.303}{t} \log \frac{D_i - D_f}{D - D_f}$$

where D_f = optical density at infinite time, D_i = initial optical density, and D = optical density at time t .

The hydrolysis of 2-methylthiazoline in alkaline solution at 78° was carried out using the sealed-ampoule technique previously described.⁴⁹ The quenched re-

action mixture was acidified with aqueous HCl and the absorbance of remaining thiazolinium ion was measured immediately at 275 m μ . Alternatively, the decrease in absorbance at 250 m μ was measured on the sample prior to acidification. Rate constants were calculated from the integrated first-order rate equation; the results of measurements at the two wave lengths were in good agreement.

pK Determinations. With the exception of the *p*-nitro-substituted derivatives, the ultraviolet spectra of the thiazolines of this study exhibit pronounced bathochromic shifts upon protonation (Table II). The changes in absorbance of thiazoline solutions as a function of pH were measured at a suitable wave length (Table II, last column) and the resulting data were fitted to the Henderson–Hasselbalch expression. The calculated pK values are listed in Table I. The increase in extinction near the wave length of maximum absorption which occurred upon protonation of the *p*-nitrophenylthiazolines **1** and **7** allowed spectrophotometric determination of their pK also.

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(49) G. L. Schmir and C. Zioudrou, *Biochemistry*, **2**, 1305 (1963).

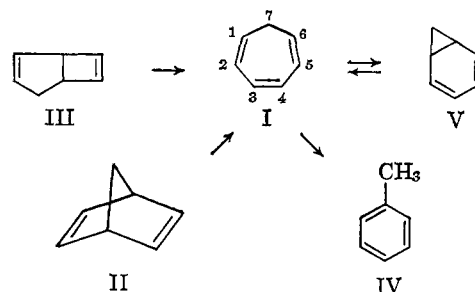
Communications to the Editor

New Thermal Rearrangements of Tropilidenes¹

Sir:

Tropilidene (I) is connected by thermal pathways of carbon skeletal rearrangement to norbornadiene (II),^{2–6} bicyclo[3.2.0]heptadiene (III),⁷ toluene (IV),^{2–6,8} and probably norcaradiene (V).^{9,10} Overlaid upon these relatively deep-seated changes are the superficial thermal 7 → 4 hydrogen shifts which disperse the hydro-

gens over the carbon framework.¹¹ We report now two new intramolecular thermal transformations of the tropilidene skeleton, one of which leads to rearranged tropilidenes and the other to 1,4-cyclohexadienes.



Although the 7 → 4 hydrogen shift can be blocked by 7,7-disubstitution, detection of a carbon skeletal rearrangement in products retaining the tropilidene ring

(1) We are indebted to the Camille and Henry Dreyfus Fund and to the Army Research Office—Durham for support of this work.

(2) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(3) W. M. Halper, G. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958).

(4) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962).

(5) K. N. Klump and J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 130 (1963).

(6) W. C. Herndon and L. L. Lowry, *ibid.*, **86**, 1922 (1964).

(7) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

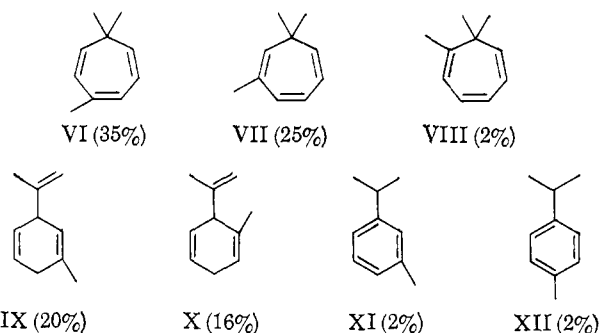
(8) Cf. also 7-methyltropilidene → ethylbenzene [A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960)].

(9) For a review, see S. J. Rhoads in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 700–703.

(10) For an example of an observably interconvertible norcaradiene–tropilidene pair, see E. Ciganek, *J. Am. Chem. Soc.*, **87**, 1149 (1965).

(11) (a) A. P. Ter Borg, H. Kloosterziel, and N. van Meurs, *Proc. Chem. Soc.*, 359 (1962); *Rec. trav. chim.*, **82**, 717 (1963), and references therein cited; (b) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962); (c) E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 59 (1964).

requires the use of an additional label. The appropriate system is provided by 3,7,7-trimethyltropilidene (VI).¹² In 40 min at 300°, VI is transformed into a mixture containing 2,7,7- and 1,7,7-trimethyltropilidenes (VII and VIII), 3- and 6-isopropenyl-1-methyl-1,4-cyclohexa-



dienes (IX and X), and *m*- and *p*-cymenes (XI and XII) in addition to recovered VI and small quantities (~2%) of unidentified substances. Very little gas or tar is formed, the material balance being essentially quantitatively accounted for by C₁₀H₁₄ products. Analyses and preparative separations of the reaction mixtures are carried out by vapor chromatography. The indicated percentage composition is approximate and is not corrected for variations in thermal conductivity. Longer heating increases the proportions of the aromatic products XI and XII.

Both kinds of nonaromatizing isomerization are reversible.¹³

The structures of VII and VIII are assigned on the basis of elemental analyses,¹⁴ ultraviolet spectra [VII, λ_{max} 270 mμ (ε 3600, 95% EtOH); VIII, λ_{max} 278 mμ (ε 4400, 95% EtOH); compare VI, λ_{max} 268 mμ (ε 4100, 95% EtOH) and other alkyltropilidenes¹⁵], and nuclear magnetic resonance (n.m.r.) spectra. Both VII and VIII show singlets of intensity 6 at 1.0 p.p.m. (methyl protons) and slightly broadened singlets of intensity 3 at 2.0 p.p.m. (allylic methyl protons). Compound VII shows multiplets at 6.4–6.2 p.p.m. (intensity 2), 6.1–5.7 p.p.m. (intensity 1), and 5.1–4.8 p.p.m. (intensity 2), all chemical shifts being measured at 60 Mc. downfield relative to tetramethylsilane as internal standard. Compound VIII shows multiplets at 6.4–6.2 p.p.m. (intensity 2), 6.1–5.7 p.p.m. (intensity 2), and 5.1–4.8 p.p.m. (intensity 1). The assignment of the absorptions in order of increasing field strength to the 3–4, 2–5, and 1–6 pairs of protons of tropilidenes is supported by the spectra of VI and at least 25 other tropilidenes of known structure.^{15,16}

Compounds IX¹⁴ and X¹⁴ show only end absorption in the ultraviolet. The n.m.r. and infrared spectra strongly suggest a close structural relationship and reveal the presence of a terminal methylene group in each (infrared λ_{max} 890 cm.⁻¹, n.m.r. broadened singlet near 4.7 p.p.m., intensity 2). Both n.m.r. spectra show three other olefinic protons, two allylic methyl groups, two

(12) Prepared by the method of E. J. Corey, H. J. Burke, and W. A. Remers, *J. Am. Chem. Soc.*, **78**, 180 (1956); cf. also J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).

(13) See the accompanying paper: J. A. Berson and M. R. Willcott, III, *ibid.*, **87**, 2752 (1965).

(14) All new compounds reported have correct empirical formulas by combustion analyses.

(15) K. Conrow, M. E. H. Howden, and D. Davis, *J. Am. Chem. Soc.*, **85**, 1929 (1963), and references cited therein.

(16) For a summary see M. R. Willcott, Ph.D. Dissertation, Yale University, 1963.

doubly allylic protons absorbing at 2.6 p.p.m., and one triply allylic proton absorbing at 3.2 p.p.m. Of the very few possible structural formulas fitting these data, mechanistic considerations¹³ suggest IX and X as the most plausible. This guess at the structures is confirmed by partial hydrogenation and tetracyanoethylene dehydrogenation of IX to *m*-cymene (XI) and of X to *o*-cymene, identification of the latter substances as well as pyrolysis products XI and XII being achieved by ultraviolet and infrared spectral comparisons with those of authentic materials.¹⁷

The occurrence of the VI ⇌ VII and VI ⇌ VIII rearrangements suggests the possibility that hitherto unsuspected skeletal reorganizations may lurk beneath the apparently undisturbed aspect of tropilidene itself when it is recovered "unchanged" from pyrolyses. This is being investigated.

(17) "Catalog of Infrared Spectrograms," and "Catalog of Ultraviolet Absorption Spectrograms," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

(18) National Institutes of Health Postdoctoral Fellow, 1964–1965.

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Skeletal Reorganization in Tropilidene Rearrangements¹

Sir:

The mechanism of the isomerization of 3,7,7-trimethyltropilidene (VI)² to 2,7,7- and 1,7,7-trimethyltropilidenes (VII and VIII) is revealed by deuterium-labeling experiments as a true skeletal reorganization of the ring carbons rather than a superficial series of methyl shifts.

Lithium aluminum hydride reduction of trideuterio-eucarvone (XIII)^{3,4} followed by dehydration with sulfuric acid⁵ gives 1,5-dideuterio-3,7,7-trimethyltropilidene (VI-*d*₂). The olefinic proton region of the n.m.r. spec-



trum of undeuterated VI, which consists of a complex multiplet of intensity 3 between 5.8 and 6.3 p.p.m. and a pair of doublets of intensity 2 near 5.0 p.p.m., is replaced in VI-*d*₂ by three broadened singlets, each of intensity 1, at 6.3, 5.9, and 5.0 p.p.m.

Pyrolysis of VI-*d*₂ under the previously described² conditions gives a mixture of VI-*d*₂ with unchanged infrared and n.m.r. spectra and the dideuterated products shown. Reversibility of both types of rearrangement with complete retention of the labeling pattern is demonstrated by pyrolysis of VII-*d*₂ or X-*d*₂ and resolution of VI-*d*₂ from the resulting product mixture. The positions of the deuteriums are assigned by n.m.r. spectro-

(1) We are indebted to the Camille and Henry Dreyfus Fund and to the Army Research Office—Durham for support of this work.

(2) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **87**, 2751 (1965). The numbering of structural formulas used in the companion paper is retained here.

(3) E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, **78**, 180 (1956).

(4) The n.m.r. spectrum is consistent with the previous³ structural assignment.