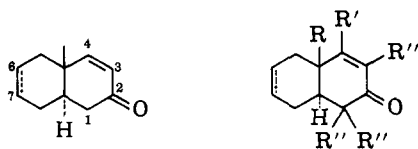


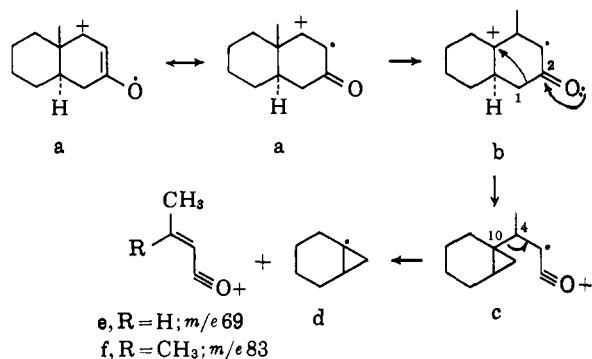
IIIb,⁹ from which we conclude that C-3, but not C-1, is implicated in the ion under question. Carbon atoms 2, 3, and 4 and their attached oxygen and hydrogen atoms correspond to C₃H₂O, leaving the elements of CH₃ unaccounted for. That these are derived from the angular methyl group could be demonstrated unambiguously by the synthesis¹⁰ of *trans*- $\Delta^{3,6}$ -10-trideuteriomethyl-2-octalone (IV), whose mass spectrum displayed an intense *m/e* 72 rather than *m/e* 69 peak.



Ia, without 6-7 double bond
b, with 6-7 double bond

II, R = CH₃, R' = D, R'' = H
III, R = CH₃, R' = H, R'' = D
IV, R = CD₃, R' = R'' = H
V, R = R' = CH₃, R'' = H
VI, R = CH₃, R' = CD₃, R'' = D

A plausible path for the abundant formation of the ion of mass 69 may be visualized through intermediacy of a molecular ion¹¹ a, in which one of the π -electrons of the double bond had been removed to furnish an "ionized double bond." Migration of the angular methyl group to b, followed by heterolysis of the 1-2 bond (c) and homolysis of the 4-10 linkage, would then yield the highly stabilized conjugated oxonium ion e (*m/e* 69) and a neutral radical, which may be represented by structure d. The major driving force for this process is probably not the conversion of a secondary (a) to a tertiary (b) carbonium ion but rather the formation of the energetically favored ion by what may well be a concerted process. The justification for this statement is that the base peak in the mass spectrum of the higher homolog, *trans*- $\Delta^{3,6}$ -4,10-dimethyl-2-hexalone (V),¹² is found at *m/e* 83 and can be attributed to structure f, since a shift to *m/e* 87 is encountered in the



(9) Prepared by heating under reflux for 20 hr. the appropriate ketone with sodium in methanol-O-*d* and heavy water. See R. H. Shapiro, J. M. Wilson, and C. Djerassi, *Steroids*, **1**, 1 (1963).

(10) The magnesium salt of cyclohexanone cyclohexylimine was alkylated (see G. Stork and S. R. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963)) with trideuteriomethyl iodide (F. A. Cotton, J. H. Fassnacht, W. D. Harrocks, and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959)), and the resulting 2-trideuteriomethylcyclohexanone was converted (J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964)) to $\Delta^{1(9)}$ -10-trideuteriomethyl-2-octalone. Reduction with lithium in liquid ammonia, bromination at C-3, and dehydrobromination (for unlabeled analog see C. Djerassi and D. Marshall, *J. Am. Chem. Soc.*, **80**, 3986 (1958)) provided the desired labeled octalone IV.

(11) For details of this approach and description of symbolism (fish-hook = one-electron shift; arrow = two-electron movement) see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. II, Holden-Day, Inc., San Francisco, Calif., 1964, pp. 1-3.

(12) L. H. Zalkow, F. X. Markley, and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 6354 (1960).

mass spectrum of the *d*₆-labeled analog VIb.⁹ No particularly favorable driving force can be ascribed to the methyl migration step (a \rightarrow b) *per se* in a molecular ion of V analogous to a.

Work is currently under way in our laboratory to examine the scope and possible generality in mass spectrometry of the presently described methyl migration. We are indebted to Dr. D. A. Lightner and Mr. John Smith, respectively, for the high- and low-resolution mass spectra.

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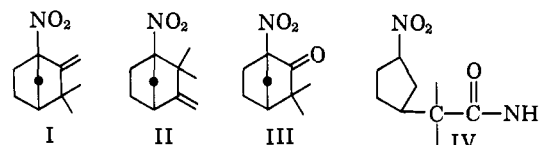
Received January 27, 1965

Deamination of 1-Amino-3,3-dimethylbicyclo[2.2.1]heptan-2-ol

Sir:

Photochemical reactions¹⁻⁵ have provided the only route to bicyclo[2.1.1]hexane derivatives. The deamination of bicyclic amines⁶ has provided an abundance of molecular rearrangements, and we wish to report the rearrangement of the amino alcohol VI to 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde (VII). Syntheses of highly strained cyclic systems by the deamination of 2-aminocyclohexanols have not been reported, although the reaction has been observed in medium-ring compounds.⁷ Reactions of 1-nitrocamphene (I),⁸ an important intermediate in our work, have been described recently, which prompts our report.

The Wagner-Meerwein rearrangement of 2-bromo-2-nitrobornane with silver nitrate was discovered by Forster,⁹ and Asahina¹⁰ assumed the product to be 1-nitrocamphene. The product of the rearrangement⁹ is isolated in low yield (40%). In addition to the evidence presented by Lipp¹¹ for the structure of the product, which does not exclude the isomer II, the hitherto unknown nitro ketone III has been isolated



from the ozonization of 1-nitrocamphene in chloroform at 0°, 90% yield, m.p. 96-97.2°; [α]²⁴_D +89.0° (*c* 5.00,

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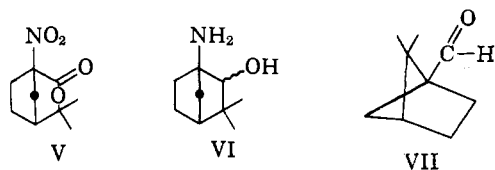
(9) M. O. Forster, *J. Chem. Soc.*, **75**, 1141 (1899); **79**, 644 (1901); **81**, 264 (1902).

(10) Y. Asahina and K. Yamaguchi, *Ber.*, **71**, 318 (1938).

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benzene); infrared spectrum (CHCl_3): 5.70 (carbonyl) and 6.55, 7.30 μ (nitro group). *Anal.* Calcd. for $\text{C}_9\text{H}_{13}\text{NO}_3$: C, 59.00; H, 7.16; N, 7.64. Found: C, 58.97; H, 7.27; N, 7.68. The nitro ketone was remarkably unstable to strong acids or bases, and a dilute solution of ammonia in cold, anhydrous ethanol rapidly converted the ketone to the amide IV, 55% yield, m.p. 114–116.5°. *Anal.* Calcd. for $\text{C}_9\text{H}_{16}\text{N}_2\text{O}_3$: C, 53.97; H, 8.09; N, 13.98; O, 23.96. Found: C, 54.22; H, 8.10; N, 13.80; O, 24.16. The ease with which the cleavage was accomplished indicates that the compound is an α -nitro ketone and not the ketone derived from the isomer II. Baeyer–Villiger oxidation of the nitro ketone III with peracetic acid gave the lactone V, 40% yield, m.p. 147.2–149.2°; $[\alpha]^{23\text{D}} +92.5^\circ$ (*c* 5.13, chloroform); infrared spectrum (CHCl_3): 5.72, 8.51 (lactone), and 6.45, 7.28 μ (nitro group). *Anal.* Calcd. for $\text{C}_{19}\text{H}_{13}\text{NO}_4$: C, 54.26; H, 6.58; N, 7.03; O, 32.13. Found: C, 54.47; H, 6.59; N, 7.14; O, 32.03. The n.m.r. spectrum of the lactone in CDCl_3 showed the *gem*-dimethyl group to be bonded to an oxygen atom¹² (δ 1.47, singlet, 3 H; 1.54, singlet, 3 H). The reactions of the tertiary nitro ketone differ markedly from the properties of a secondary nitro ketone.¹³

Catalytic reduction of the ketone III with platinum and hydrogen in glacial acetic acid gave the amino alcohol VI, 61% yield, m.p. 99–101.2°; $[\alpha]^{23\text{D}} -10.3^\circ$



(*c* 5.07, ethanol). *Anal.* Calcd. for $\text{C}_9\text{H}_{17}\text{NO}$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.69; H, 11.12; N, 9.12. The infrared spectrum showed the reduction to be complete.

Nitrous acid deamination of the amino alcohol under nitrogen yielded the aldehyde VII which was rapidly oxidized by air, m.p. 84.5–88°; $[\alpha]^{23\text{D}} -6.8^\circ$ (*c* 5.08, benzene); infrared spectrum (CCl_4): 3.58, 3.70, and 5.85 μ . Vapor phase chromatography on a silicone column indicated that the product of the reaction was homogeneous. The n.m.r. spectrum of the aldehyde in CCl_4 was similar to the spectra of bicyclo[2.1.1]hexane derivatives already reported in the literature^{14,15}: C-5- CH_3 , δ 0.92 (singlet, 3 H); C-6-*endo*-H, 1.06 (doublet, *J* = 7.5 c.p.s., 1 H); C-5- CH_3 , 1.28 (singlet, 3 H); C-2- and C-3- H_2 , 1.77 (multiplet, 4 H); C-6-*exo*-H, 2.08 (multiplet, 1 H); C-4-H, 2.33 (broad, 1 H); and C-1-CHO, 9.67 (singlet, 1 H).

The semicarbazone of the aldehyde was isolated directly from the deamination reaction in 76% yield based on the amino alcohol, m.p. 192–193.2° dec. *Anal.* Calcd. for $\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.69; H, 8.80; N, 21.58. The dimedone derivative melted at 176–178°. *Anal.* Calcd. for $\text{C}_{25}\text{H}_{36}\text{O}_4$: C, 74.96; H, 9.06; O, 15.98.

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Found: C, 74.91; H, 9.03; O, 16.01. The dimedone derivative was converted to the corresponding octahydroxanthene, m.p. 224.7–225.7° dec. *Anal.* calcd. for $\text{C}_{25}\text{H}_{34}\text{O}_8$: C, 78.49; H, 8.96; O, 12.55. Found: C, 78.75; H, 8.98; O, 12.52.

The aldehyde was oxidized with 30% hydrogen peroxide to 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylic acid, 29% yield based on the amino alcohol, m.p. 118–120.2°; $[\alpha]^{23\text{D}} +11.2^\circ$ (*c* 5.03, benzene). *Anal.* Calcd. for $\text{C}_9\text{H}_{14}\text{O}_2$: C, 70.10; H, 9.15; O, 20.75. Found: C, 70.15; H, 9.20; O, 20.72; neut. equiv., 155. The n.m.r. spectrum of the acid in CCl_4 showed that the bicyclo[2.1.1]hexane system had been retained: C-5- CH_3 , δ 0.91 (singlet, 3 H); C-6-*endo*-H, 1.14 (doublet, *J* = 7.5 c.p.s., 1 H); C-5- CH_3 , 1.28 (singlet, 3 H); C-2- and C-3- H_2 , 1.80 (multiplet, *ca.* 4 H); C-6-*exo*-H, 2.02 (multiplet, *ca.* 1 H); C-4-H, 2.29 (broad, 1 H); and C-1-COOH, 12.15 (singlet, 1 H).¹⁶

The specificity of the bond migration (C-2–C-3) to the bridgehead carbonium ion derived from the amino alcohol with the formation of the bicyclo[2.1.1]hexane system is noteworthy. The product of a hydride shift to the carbonium ion was not detected even though the resulting ketone would be less strained than the product which was actually formed. The deamination of the bridgehead amino alcohol gave the product of ring contraction in excellent yield (isolated as the semicarbazone), and we suggest that the reaction may have substantial merit for the synthesis of highly strained cyclic systems.

(16) All n.m.r. spectra were obtained with a Varian A-60 spectrometer. The chemical shifts are given in p.p.m. (δ) downfield from tetramethylsilane used as an internal reference.

(17) N.D.E.A. Fellow, 1962 to present.

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Photochemical Interactions in *ortho,ortho'*-Disubstituted Biphenyls¹

Sir:

We wish to report two new photochemical reactions involving *ortho,ortho'* interactions in the biphenyl series. Irradiation of the *p*-chlorophenyl anil of *o*-nitro-*o'*-formylbiphenyl (1), m.p. 104° (*Anal.* Calcd. for $\text{C}_{19}\text{H}_{13}\text{N}_2\text{O}_2\text{Cl}$: C, 67.76; H, 3.89; N, 8.32. Found: C, 68.70; H, 3.93; N, 8.43), in ethanol solution using a 450-w. Hanovia immersion lamp and a Corex filter, resulted in the formation of 5(6H)-phenanthridone (5), m.p. 290–292° (lit.² m.p. 290–292°) in 25% yield. Two mechanistically reasonable and sterically feasible pathways are possible for this intramolecular oxidation–reduction reaction. In path A, cycloaddition of the nitro group to the polarized anil C=N bond to give the oxadiazetidene N-oxide 2, followed by extrusion of *p*-chloronitrosobenzene, would give phenanthridine N-oxide (3),^{3,4} which we have been

(1) This work was supported in part by a grant (CA 02551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service.

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