A Synthesis of 5,5-Dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde[1]

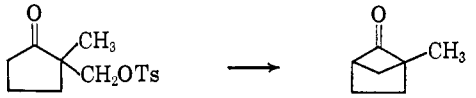
Kikuye Ebisu,[2] Leoniece B. Batty, Jane M. Higaki, and H. O. Larson

Contribution from the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822. *Received January 3, 1966*

Abstract: Conclusive evidence is presented establishing 1-nitrocamphene (**8**) as the product of the rearrangement of 2-bromo-2-nitrobornane (**7**) with silver nitrate. Deamination of the bridgehead amino alcohol **5** with nitrous acid leads to the formation of the bicyclo[2.1.1]hexane derivative **6**. The latter reaction may have considerable utility in the synthesis of other strained polycyclic systems.

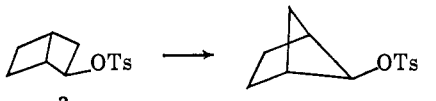
Considerable attention has been focused on the bicyclo[2.1.1]hexane system within the last decade. Bond-angle deformation studies of bridgehead substituted bicyclo[2.1.1]hexane derivatives have indicated an enhanced amount of s character in the external bridgehead orbital.[3] An unusually large spin–spin coupling across four bonds has been observed for several compounds in the series.[4,5] Synthesis of the bicyclo[2.1.1]hexane system has primarily involved photochemical ring contraction of α-diazoketones derived from bicyclo[2.2.1]heptane and bicyclo[3.1.1]-heptane by the Wolff rearrangement.[6–8] The photolytic intramolecular cycloaddition of compounds containing both conjugated and isolated double bonds[9,10] and only isolated double bonds[11] has been another route to the bicyclo[2.1.1]hexane system. Bicyclo[2.1.1]hexane derivatives have also been obtained from the mercury-photosensitized decomposition of ketones derived from bicyclo[2.2.1]heptane.[12] The latter two methods do not seem promising due to low yields of the desired bicyclo-[2.1.1]hexane derivatives and, in most cases, considerable by-product formation.

Only two instances of formation of the bicyclo-[2.1.1]hexane system by nonphotolytic methods have been reported. The ketone **2** was obtained in about 10% yield by an intramolecular cyclization of the tosylate **1** with potassium *t*-butoxide.[13] A substantial



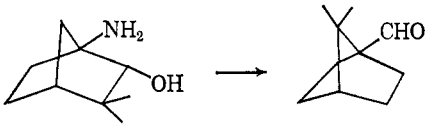
1 **2**

amount of *t*-butyl 5-methyl-5-hexenoate was also isolated. Acetolysis of the tosylate **3** resulted in a 50% yield of the bicyclo[2.1.1]hexane derivative **4**.[14] In addition a mixture of three acetates was produced.



3 **4**

The deamination of bicyclic amines has provided an abundance of molecular rearrangements,[15] and we report here a detailed description of the semipinacolic rearrangement of the 2-hydroxy amine **5** to 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde (**6**). This

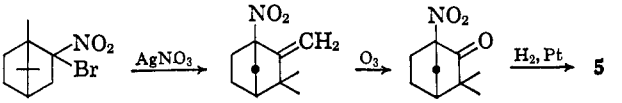


5 **6**

rearrangement constitutes a new synthetic route to the bicyclo[2.1.1]hexane system.

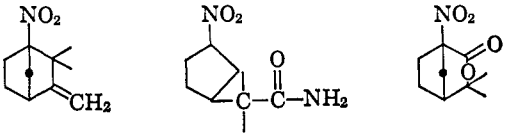
Results and Discussion

The bridgehead amino alcohol (2-hydroxyamine) **5** was synthesized according to the scheme outlined



7 **8** **9**

here. A Wagner–Meerwein rearrangement occurred upon treatment of 2-bromo-2-nitrobornane (**7**) with silver nitrate.[16,17] Chemical evidence supporting structure **8** (1-nitrocamphene) as the product of the rearrangement but not excluding the isomer **10** has been



10 **11** **12**

reported.[18] The nmr data for the rearranged product

(1) A preliminary report of this work has appeared: K. Ebisu, L. B. Batty, J. M. Higaki, and H. O. Larson, *J. Am. Chem. Soc.*, **87**, 1399 (1965).
(2) National Defense Education Act Fellow, 1962–1965.
(3) K. B. Wiberg and B. R. Lowry, *J. Am. Chem. Soc.*, **85**, 3188 (1963).
(4) J. Meinwald and A. Lewis, *ibid.*, **83**, 2769 (1961).
(5) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).
(6) L. Horner and E. Spietschka, *Ber.*, **88**, 934 (1955).
(7) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857, 5445 (1960).
(8) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3988 (1961).
(9) R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, 19, 1995 (1963).
(10) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1892 (1964).
(11) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).
(12) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).
(13) W. H. Brown, Ph.D. Thesis, Columbia University, 1959.
(14) R. N. McDonald and C. E. Reineke, *J. Am. Chem. Soc.*, **87**, 3020 (1965).
(15) J. A. Berson, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963,, p 205.
(16) M. O. Forster, *J. Chem. Soc.*, **75**, 1141 (1899); **79**, 644 (1901); **81**, 264 (1902).
(17) Y. Asahina and K. Yamaguchi, *Ber.*, 71, 318 (1938).
(18) P. Lipp and H. Knapp, *ibid.*, **73**, 915 (1940).

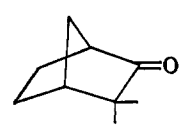
are in agreement with that reported elsewhere.[19] A six-proton singlet due to the protons of the *gem*-dimethyl group appeared at δ 1.17. Signals attributable to the protons of the exocyclic methylene group appeared at δ 4.80 and 4.85 ($J \sim 1$ cps). The remaining methylene and bridgehead protons were present as multiplets at δ 1.70–2.65. Direct chemical and physical evidence has now been obtained which proves that 1-nitrocamphene (**8**) is the product of the rearrangement. Conversion of 2-bromo-2-nitrobornane to 1-nitrocamphene with silver nitrate provides a new route to bridgehead nitro compounds and bridgehead amines which, with the exception of 1-nitroadamantane and 1-nitrobicyclo[2.2.1]heptane, are not available by nitration.[20,21]

Ozonization of the rearranged product in chloroform at 0° afforded the nitro ketone **9** in 91% yield. The infrared spectrum showed a band at 5.70 μ, which is characteristic for the carbonyl group, and absorption at 6.55 and 7.30 μ, which is typical for the nitro group. The nmr spectrum of the nitro ketone exhibited sharp, three-proton singlets at δ 1.16 and 1.22 due to the protons of the *gem*-dimethyl group. A cold, dilute solution of ammonia in ethanol rapidly converted the nitro ketone to the amide **11** in 55% yield. Appearance of absorption in the infrared spectrum at 6.05 and 6.20 μ confirmed the formation of an amide. The amide was soluble in 10% sodium hydroxide solution. That the product of the ozonization was an α-nitro ketone and not the ketone derived from compound **10** was indicated by the ease with which cleavage in ammonia was accomplished and by the instability of the nitro ketone in strong acid or base.

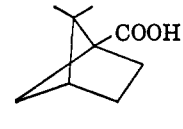
Baeyer–Villiger rearrangement of the nitro ketone **9** with peracetic acid yielded the lactone **12** in 39% yield. Bands in the infrared spectrum at 5.72 and 8.51 μ substantiated the formation of a lactone. Sharp, three-proton singlets at δ 1.46 and 1.53 attributable to the protons of the *gem*-dimethyl group were present in the nmr spectrum of the lactone. The large downfield shift, about 0.3 ppm, relative to the methyl proton resonance signals of the nitro ketone **9** indicated that the *gem*-dimethyl group of the lactone **12** is adjacent to oxygen.[22]

Reduction of the nitro ketone **9** with hydrogen using platinum as catalyst afforded the bridgehead amino alcohol **5** in 61% yield. The hydroxyl group is assigned the *endo* configuration on the assumption that hydrogen attack at the carbonyl group of the nitro ketone **9** would occur predominantly from the less hindered *exo* side. The assignment is in accord with results obtained from a study of the catalytic reduction of a structurally related compound, camphenilone (**13**),[23] in which an epimeric mixture containing 85% of the *endo* alcohol was isolated.

Deamination (semipinacolic rearrangement) of the amino alcohol **5** with nitrous acid yielded the aldehyde **6** which was rapidly oxidized by air. Absorption



13



14

bands in the infrared spectrum at 3.58, 3.70, and 5.85 μ indicated the presence of a formyl group, and bands at 7.21 and 7.30 μ, the presence of a *gem*-dimethyl group. Structural similarity of the aldehyde with known bicyclo[2.1.1]hexane derivatives was evidenced by its nmr spectrum:[5,10,12] C_5CH_3, δ 0.92 (singlet); C_6-*endo*-H, 1.06 (doublet, J = 7.5 cps); C_5CH_3, 1.28 (singlet); C_2- and C_3H_2, 1.77 (multiplet); C_6-*exo*-H, 2.08 (multiplet); C_4H, 2.33 (broad); and C_1CHO, 9.67 (singlet). The distinguishing feature of the spectrum was the high-field doublet centered at δ 1.06, which is attributable to geminal coupling of the C_6 *endo* and *exo* protons. The magnitude of the coupling constant (7.5 cps) is of the order observed for bicyclo[2.1.1]-hexane derivatives. The multiplet at δ 1.77 approximates an A_2B_2 system. That the formyl group is located at a bridgehead position was indicated by the singlet at δ 9.67.

The product of the deamination was found to be homogeneous by vapor phase chromatography on a silicone column. The possibility that traces of other products were formed is not excluded. In order to determine the extent of ring contraction, the semicarbazone of the aldehyde was prepared directly from the deamination reaction medium. The yield of semicarbazone (mp 192–193.2° dec) based on the amino alcohol **5** was 76%.

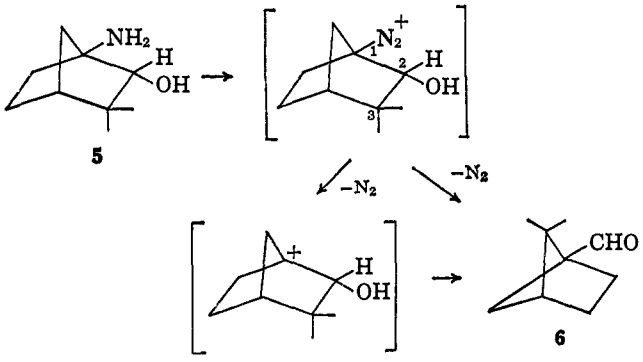
Oxidation with 30% hydrogen peroxide converted the aldehyde **6** to the acid **14** in 29% yield based on the amino alcohol. The nmr spectrum of the acid **14** was similar to that of its precursor, aldehyde **6**: C_5CH_3, δ 0.91 (singlet); C_6-*endo*-H, 1.14 (doublet, J = 7.5 cps); C_5CH_3, 1.28 (singlet); C_2- and C_3H_2, 1.80 (multiplet); C_6-*exo*-H, 2.02 (multiplet); C_4H, 2.29 (broad); and C_1COOH, 12.15 (singlet). The assignments for the C_6-*exo* and C_4 bridgehead protons of the aldehyde and acid are tentative, although one would expect the C_4 proton to resonate futher downfield than the C_6-*exo* proton.[5]

Condensation of the aldehyde **6** with 5,5-dimethylcyclohexane-1,3-dione gave the dimedone derivative, which was converted to the corresponding octahydroxanthene in the usual manner. These derivatives, together with the acid formed by oxidation, must be derived from an aldehyde.

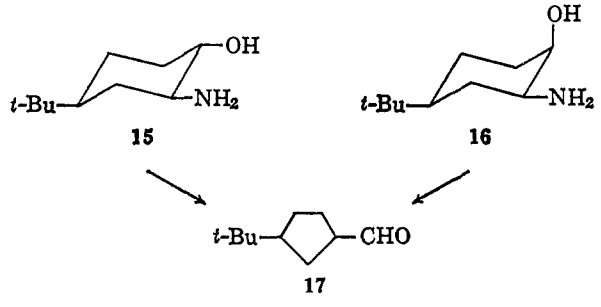
The only product detected in the deamination of the amino alcohol **5** was the ring-contracted aldehyde **6**. Migration of the C_2–C_3 electron pair to the C_1 bridgehead position probably occurred simultaneously with or immediately after elimination of nitrogen.[24] The product of a 1,2-hydride shift was not obtained, although the resulting ketone **13** would have been less strained than 6, the product of ring contraction. It is interesting to note that the aldehyde **6** was formed with inversion of configuration at the C_1 bridgehead center. The C_2–C_3 electron pair must approach the C_1 bridgehead atom from the side opposite the position

(19) Y. Brunel, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 1895 (1964).
(20) G. W. Smith, *J. Am. Chem. Soc.*, 81, 6319 (1959), and references cited therein.
(21) G. W. Smith and H. D. Williams, *J. Org. Chem.*, 26, 2207 (1961).
(22) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 53.
(23) W. Hückel, D. S. Nag, and R. Zeisberger, *Ann.*, 645, 101 (1961).
(24) J. G. Traynham and M. T. Yang, *J. Am. Chem. Soc.*, 87, 2394 1965).

temporarily occupied by the diazonium group (backside attack) since no other direction of approach is geometrically possible.



Formation of the highly strained aldehyde **6** is plausible in view of the fact that an *anti* and nearly coplanar relationship exists with the C_2–C_3 and C_1–N bonds of the diazonium intermediate. The synthesis and deamination of the four epimeric 4-*t*-butyl-2-aminocyclohexanols have been described recently.[25,26] It was reported that the deamination of the four conformationally homogeneous amino alcohols is highly stereoselective leading in each instance to the expected product. The sole product detected in the deamination of amino alcohols **15** and **16** (note *anti* relationship of C_1–C_6 and C_2–N bonds) was the ring-contracted aldehyde **17**. Similarly the deamination of



trans-2-aminocyclohexanol (diequatorial conformation preferred) has been found to yield almost exclusively the ring-contracted aldehyde, cyclopentylmethanal.[27] Deamination of the *trans* compound of the next higher homolog, 2-aminocycloheptanol, also resulted in ring contraction.[28]

Experimental Section

All melting points are corrected. Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institute, Mülheim, Germany. Infrared spectra were recorded with a Beckman IR5 spectrophotometer. Nmr spectra were recorded and integrated on a Varian A-60 nmr spectrometer. Chemical shifts are given in ppm (δ) downfield from tetramethylsilane as the internal reference.

1-Nitrocamphene (8). A solution of 2-bromo-2-nitrobornane[16] (**7**, 30 g, 0.114 mole) in 200 ml of ethanol was heated to reflux temperature. Silver nitrate (50 g, 0.294 mole) was added in small amounts. The mixture was protected from light and was refluxed vigorously with stirring for 27 hr. The silver bromide and excess silver nitrate were filtered off, and the residue, after removal of solvent, was steam distilled. Extraction of the distillate with ether[29] followed by evaporation of solvent afforded an oil which crystallized in the minimum amount of ethanol. The product **8** (9.11 g, mp 50–54°) was obtained in 44% yield (lit.[16] 50%) and after one recrystallization exhibited mp 54.2–55.6° (lit.[16] mp 56°); nmr spectrum ($CDCl_3$) δ 1.17 (singlet, 6 H), 1.70–2.65 (multiplets, 7 H), 4.80 (doublet, J = *ca.* 1 cps, 1 H), and 4.85 (doublet, J = *ca.* 1 cps, 1 H).

3,3-Dimethyl-1-nitrobicyclo[2.2.1]heptan-2-one (9). A solution of 1-nitrocamphene (**8**, 14.8 g, 0.0814 mole) in chloroform (150 ml) was treated with ozone (*ca.* 0.12 mole/hr) for 2 hr at 0° and 1 hr at room temperature. Water (100 ml) was added, and the resulting mixture was refluxed for 40 min. Extraction with chloroform followed by the usual work-up gave the nitro ketone **9** (13.5 g, mp 90–94°) in 91% yield. The melting point was raised to 96–97.2° after recrystallization from ethanol; $[\alpha]^{24}D$ +89.0° (*c* 5.00, benzene); infrared spectrum ($CHCl_3$) 5.70 (carbonyl) and 6.55, 7.30 μ (nitro group); nmr spectrum ($CDCl_3$) δ 1.16 (singlet, 3 H), 1.22 (singlet, 3 H), and 1.70–2.90 (multiplets, 7 H).

Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.16; N, 7.64. Found: C, 58.97; H, 7.27; N, 7.68.

2,2-Dimethyl-2-(3′-nitrocyclopentyl)acetamide (11). Ammonia was bubbled through ethanol (50 ml) at 0° for 2 min. The nitro ketone **9** (1.6 g, 0.0089 mole) was added, and the solution was shaken and left to stand overnight at room temperature. A white precipitate appeared, which was recrystallized from ethanol. The amide (1.0 g, 55%) exhibited mp 113–114.5°. After four recrystallizations, the amide had mp 114.5–116°, $[\alpha]^{22}D$ 0° (*c* 5.15, acetonitrile), infrared spectrum (KBr) 6.05 and 6.20 μ (amide).

Anal. Calcd for $C_9H_{16}N_2O_3$: 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.

4,4-Dimethyl-1-nitro-3-oxabicyclo[3.2.1]octan-2-one (12). Using a modification of the method of Meinwald and Frauenglass,[30] the nitro ketone **9** (3.00 g, 0.0164 mole) in 30 ml of glacial acetic acid was added to a cold solution of 30% hydrogen peroxide (10 ml, 0.098 mole) and acetic acid (10 ml). An additional 35 ml of acetic acid and anhydrous sodium acetate (1.50 g, 0.0183 mole) was added. The solution was kept in the dark for 9 days. The solution of the lactone **12** was cooled to 0°, and a cold solution of sodium carbonate (70 g in 300 ml of water) was added. Extraction with chloroform followed by the usual work-up afforded a white solid which was recrystallized from ethanol (1.29 g, 39%), mp 140–145°. After further recrystallization, the lactone exhibited mp 147.2–149.2°; $[\alpha]^{23}D$ +92.5° (*c* 5.13, chloroform); infrared spectrum ($CHCl_3$) 5.72, 8.51 (lactone), and 6.45, 7.28 μ (nitro group); nmr spectrum ($CDCl_3$) δ 1.46 (singlet, 3 H), 1.53 (singlet, 3 H), and 1.95–3.10 (multiplets, 7 H).

Anal. Calcd for $C_9H_{13}NO_4$: 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.

1-Amino-3,3-dimethylbicyclo[2.2.1]heptan-2-ol (5). The bridgehead amino alcohol **5** was prepared by the method of Kornblum and co-workers.[31] A mixture of the nitro ketone **9** (9.30 g), glacial acetic acid (52 ml), and platinum dioxide (1.78 g) was shaken with hydrogen (45 psi) at room temperature. After 42 hr the mixture was filtered, and most of the acetic acid was removed by freeze drying the filtrate. The residue was made basic with sodium carbonate and then strongly basic with 20% sodium hydroxide solution. The solid obtained after thorough extraction of the basic solution with chloroform was recrystallized from hexane. The amino alcohol **5** (first crop, 5.40 g, 68%, mp 91–97°) was soluble in water and sublimed readily. After another recrystallization, the alcohol (4.85 g, 61%) had mp 98–100.5°. An analytical sample exhibited mp 100–102°, $[\alpha]^{23}D$ −10.3° (*c* 5.07, ethanol).

Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.69; H, 11.12; N, 9.12.

The white solid recovered from the filtrate of the first crop was sublimed under reduced pressure at 50–60°. The sublimed material (0.760 g) exhibited mp 63–93.5°.

5,5-Dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde (6). The method of McCasland[27] was followed. A 4 *m* sodium nitrite solution (7.5 ml, 8.54 g of solution, 0.0267 mole) was added dropwise with stirring to a solution containing the amino alcohol **5** (0.805 g, 0.00518 mole) and acetic acid (20 ml of a 50% solution). The mixture was stirred under nitrogen at room temperature for 55 min, neutralized with sodium carbonate in the cold, saturated

(25) J. Sicher, F. Šipoš, and M. Tichý, *Collection Czech. Chem. Commun.*, **26**, 847 (1961).

(26) M. Chérest, H. Felkin, J. Sicher, F. Sipoš, and M. Tichý, *J. Chem. Soc.*, 2513 (1965).

(27) G. E. McCasland, *J. Am. Chem. Soc.*, **73**, 2293 (1951).

(28) J. W. Huffman and J. E. Engle, *J. Org. Chem.*, **24**, 1844 (1959).

(29) All organic extracts were dried over anhydrous magnesium sulfate.

(30) J. Meinwald and E. Frauenglass, *J. Am. Chem. Soc.*, **82**, 5235 (1960).

(31) N. Kornblum, W. D. Gurowitz, H. O. Larson, and D. E. Hardies, *ibid.*, **82**, 3099 (1960).

with sodium chloride, and filtered. Anhydrous magnesium sulfate was added to the crude aldehyde **6**, and the mixture was sublimed under reduced pressure at room temperature. Cold water (*ca.* 5°) was introduced into the cold finger of the sublimator. The sublimed aldehyde was a colorless, waxy solid which had mp 84.5–88°; $[\alpha]^{23}D$ −6.8° (*c* 5.08, benzene); infrared spectrum (CCl_4) 3.58, 3.70, 5.85 (formyl group), and 7.21, 7.30 μ (*gem*-dimethyl group); nmr spectrum (CCl_4) 0.92 (singlet, 3 H), 1.06 (doublet, J = 7.5 cps, 1 H), 1.28 (singlet, 3H), 1.77 (multiplet, 4 H), 2.08 (multiplet, 1 H), 2.33 (broad, 1 H), and 9.67 (singlet, 1 H).

A sample of the sublimed material in carbon tetrachloride was found to be homogeneous by vpc (temperature programmed from 125 to 250°, 5-ft column packed with 20% silicone Ge-SF-96 on 60–80 mesh firebrick). The crude material was also homogeneous by vpc analysis. An attempt to prepare the *p*-nitrobenzoate of any alcoholic product in the filtrate from the crude aldehyde yielded negative results.

Semicarbazone of Aldehyde 6. The aldehyde **6** was prepared from the amino alcohol **5** (0.500 g, 0.00322 mole) as described previously using sodium nitrite (5 ml of a 4 *m* solution, 0.0181 mole) and acetic acid (15 ml of a 50% solution). Ethanol (15 ml) was added to the reaction medium.[32] The solution was shaken vigorously after addition of semicarbazide hydrochloride (0.520 g, 0.00465 mole) and sodium acetate trihydrate (0.800 g, 0.00588 mole). A white, powdery solid appeared within 2 min. The semicarbazone (0.480 g, mp 189–191° dec) was obtained in 76% yield based on the amino alcohol **5**. An analytical sample was prepared after three recrystallizations from ethanol–water, yielding colorless needles, mp 192–193.2° dec.

Anal. Calcd for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.69; H, 8.80; N, 21.58.

5,5-Dimethylbicyclo[2.1.1]hexane-1-carboxylic acid (14). The crude aldehyde **6** (prepared in the manner described previously using 1.00 g of amino alcohol **5**, 9 ml of a 4 *m* sodium nitrite solution, and 25 ml of a 50% acetic acid solution) was added gradually to a solution of sodium hydroxide (8 ml of a 5% solution) and hydrogen peroxide (4 ml of a 30% solution) which had been heated to 65–70° in a water bath.[32] The mixture was shaken and kept at 65–70° for 20 min. Another 3 ml of 30% hydrogen peroxide was added during the reaction. The solution was acidified to congo red, and the white solid which precipitated was removed by filtration. The acid **14** (0.287 g, mp 115–119°) was obtained in 29% yield based on the amino alcohol **5**. After sublimation under reduced pressure at 50–60°, the acid exhibited mp 120.2–122.2°; $[\alpha]^{23}D$ +11.2° (*c* 5.03, benzene); infrared spectrum (CCl_4) 3.0–4.2, 5.90 (carboxyl group), and 7.21, 7.29 μ (*gem*-dimethyl group); nmr spectrum (CCl_4) 0.91 (singlet, 3 H), 1.14 (doublet, J = 7.5 cps, 1 H), 1.28 (singlet, 3 H), 1.80 (multiplet, *ca.* 4 H), 2.02 (multiplet, *ca.* 1 H), 2.29 (broad, 1 H), and 12.15 (singlet, 1 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15; O, 20.75. Found: C,70.15; H, 9.20; O, 20.72; neut equiv, 155.

Dimedone Derivative of Aldehyde 6. The crude aldehyde **6** (prepared as described previously using 0.500 g of amino alcohol **5**, 5 ml of a 4 *m* sodium nitrite solution, and 15 ml of a 50% acetic acid solution) was dissolved in 10 ml of 70% ethanol.[32] The solution was added gradually to a hot solution of dimedone (0.398 g, 0.00284 mole), ethanol (15 ml of a 70% solution), and piperidine (2 drops). The resulting solution was heated at *ca.* 75° for 8 min. One milliliter of water was added, and the solution was left to stand at room temperature overnight and white crystals appeared. The dimedone derivative (0.198 g, mp 170–173.5°) was obtained in 15% yield based on the amino alcohol **5**. An analytical sample was prepared after four recrystallizations from 70% ethanol, mp 176–178°.

Anal. Calcd for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06; O, 15.98. Found: C, 74.91; H, 9.03; O, 16.01.

Octahydroxanthene Derivative of Aldehyde 6. Concentrated hydrochloric acid (2 drops) was added to a solution of the dimedone derivative of **6** (0.157 g) in 13 ml of 80% ethanol.[32] The mixture was heated at *ca.* 80° for 10 min. One milliliter of 80% ethanol and another drop of hydrochloric acid were added during the reaction. Water was added to the cloud point, and the mixture was kept in the cold. The white octahydroxanthene derivative (0.125 g, 83%, mp 222.4–223.2° dec) was recovered by filtration. After four recrystallizations from methanol–water, the derivative exhibited mp 224.7–225.7° dec.

Anal. Calcd for $C_{25}H_{34}O_3$: C, 78.49; H, 8.96; O, 12.55. Found: C, 78.75; H, 8.98; O, 12.52.

(32) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956.

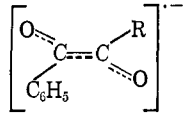
Semidiones. I. Acyclic Semidione Radical Anions and Cations Containing a Single Aryl Substituent[1]

Glen A. Russell, E. Thomas Strom,[2a] Erach R. Talaty, and Steven A. Weiner[2b]

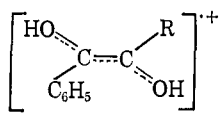
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa. *Received December 20, 1965*

Abstract. The preparation of a number of semidione radical anions ($ArC(O^-)=C(O\cdot)R$) and the analysis of their well-resolved esr spectra are reported. Less highly resolved spectra are reported for some of the corresponding diprotonated derivatives ($ArC(OH)-C^+(OH)R$).

Acyclic semidione radical anions ($RC(O\cdot)=(O^-)R$) or radical cations ($RC(OH)-C^+(OH)R$) can be detected by electron spin resonance (esr) spectroscopy under a variety of reaction conditions. We now report details on the preparation, detection, and esr spectral analysis of a series of radical anions (**1**) and cations (**2**) with 1-aryl substituents.



1a, R=H



2a, R=H

The parent molecules (R = H) of series **1** and **2** have both been prepared. Reduction of anhydrous phenylglyoxal in 98% sulfuric acid by sodium dithionite gives rise to a radical cation presumed to be **2a**. The esr spectrum (Figure 1) shows a doublet splitting of a^H = 3.14 gauss. The *p*-bromo, *p*-methyl, and *p*-methoxy

(1) Reactions of Resonance Stabilized Anions. XXI. This work was supported by grants from the Petroleum Research Fund and the National Science Foundation.

(2) (a) National Institutes of Health Predoctoral Fellow, 1962–1963; (b) National Aeronautics and Space Administration Predoctoral Fellow, 1964–1965.