corresponding diones **11b** and **c**, after the solution was refluxed about 20 and 30 hr, respectively. In each case, infrared spectra of the crystalline crude product, obtained after evaporation to dryness, were identical with those of the pure diones, indicating that the conversions are essentially quantitative.

When the progress of hydrolysis was carefully monitored in the infrared region, plots of A_1/A_2 were found to be linear with time in the range of 30–70% reaction, as determined by comparison with spectra of standard mixtures of reactant and product, where A_1 and A_2 are the carbonyl absorbancies of product (at ~5.82 μ) and reactant (at ~5.92 μ), respectively. This finding simplified the conversion of absorbancy ratios of known 1:1 mixtures into half-lives of reaction. The experiments were carried out on approximately 20 mg of photoadduct in a solution of acetonitrile (4 ml) and water (2 ml) heated at reflux in an oil bath held at 105°. Under these conditions, the half-lives of reaction were found to be 27.5, 168, and 252 min for **7a, b, and c**, respectively.

1,2-Diphenyl-3a-acetoxy-3,3a,8,8a-tetrahydrocyclopent[*a*]indene-3,8-dione (11a-OAc).—A solution of the diphenyldione **11a** (220 mg) in pyridine (1.5 ml) and acetic anhydride (0.1 ml) was stirred at room temperature for 2 days and then poured into an ice–water mixture. The resulting precipitate (250 mg) was collected and recrystallized from acetone–hexane solution to provide 206 mg (84% yield) of **11a**-OAc, mp 173–174°.

Deuterium Exchange Experiment with 1-Methyl-2-phenyl-3a-hydroxy-3,3a,8,8a-tetrahydrocyclopent[*a*]indene-3,8-dione (11c).—A solution of the methylphenyldione **11c** (111 mg) in dioxane (5.5 ml) and D_2O (1.5 ml) was refluxed for 90 hr and then evaporated to dryness. The resulting solid was taken up in benzene, which was washed with water and dried. After removal of the benzene and recrystallization from benzene–hexane solution, 108 mg of colorless crystals, mp 176–177°, were isolated and shown to be the tetradeuterio analog of **11c**, in which the methyl and methine hydrogens had been replaced by deuterium atoms, on the basis of infrared, ultraviolet, nmr, and mass spectra. The mass spectrum exhibited molecular ions for only tri- (*m/e* 294) and tetradeuterated (*m/e* 295, base peak) material in the ratio of 1:7 indicating that more than 85% of the material was tetradeuterated.

Registry No.—**5a**, 16343-59-2; **5a** (ethanolysis product), 18945-02-3; **5b**, 16343-60-5; **5c**, 18926-54-0; **7a**, 16526-86-6; **7b**, 18926-56-2; **7c**, 18926-57-3; **11a**, 18926-58-4; **11a** (acetylated), 18926-59-5; **11b**, 18926-60-8; **11c**, 18926-61-9; **19**, 18926-62-0; **21**, 18926-30-2.

Synthesis and Deamination of 1-Amino-4-bromo-7,7-dimethylbicyclo[2.2.1]heptan-2-ol

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Received September 26, 1968

Deamination of the amino alcohol **9** leads to the formation of the bicyclo[2.1.1]hexane derivative **10**. The amine **9** is available from the degradation of **2**. Lead tetraacetate oxidation of the semicarbazone **6** yields the novel heterocycle **7** that hydrolyzes remarkably easily to the amine.

Interest in the chemistry of small cyclic systems remains at a high level.[4] The synthesis of bicyclo[2.1.1]hexane and its derivatives employs photochemical reactions almost exclusively. The photochemical cyclization of 1,5-hexadiene[5] and related 1,5-hexadienes[6–8] is an expeditious route which has been exploited recently. Photosensitized internal cycloaddition reactions of suitably constituted dienes may provide the best method for the synthesis of the bicyclo[2.1.1]hexane ring system.[9,10] The observation, "there is considerable need for additional synthetic methods to the bicyclo[2.1.1]hexane system from commercial starting materials and by procedures which can be operated on a reasonable scale,"[8] is relevant. The rearrangement of the amino alcohol **1** to 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde on treatment with nitrous acid may have been due to a fortunate choice for the migrating group.[11] The deamination of a similarly constituted amino alcohol unsubstituted at C-3 would determine the scope of the reaction.

The amide **2** appeared to be useful for our objective,[12] and oxidation of the corresponding nitrile with alkaline hydrogen peroxide furnished the requisite amide; usual hydrolytic procedures fail to produce the amide.[13] Treatment of **2** with alkaline sodium hypobromite resulted in the heterocycle **3**. Formation of the cyclic compound in the Hofmann reaction from the intermediary isocyanate is similar to the formation of cyclic urethans in the Curtius degradation of β-hydroxy acid azides.[14] The conversion of **3** into an amino alcohol proved to be arduous.

The cyclic urethan **3** was converted to a neutral compound, $C_9H_{13}BrO$, which was devoid of nitrogen, by the action of hot sulfuric acid. Absorption bands in the infrared (ir) spectrum at 7.22 and 7.33 μ indicated that the *gem*-dimethyl group had been retained. The characteristic absorption of a carbonyl group in a five-membered ring was observed at 5.70 μ. The nuclear magnetic resonance (nmr) spectrum required that the bromine atom be attached to a tertiary carbon atom. Structure **4** was tentatively assigned to the product. Cleavage of a C–N bond at the bridgehead position is surprising. The reaction appears to be a

(1) East–West Center Grantee, 1965 to present.

(2) We appreciate the support of National Science Foundation Grant No. GE-3107.

(3) N.D.E.A. Fellow, 1962 to 1965.

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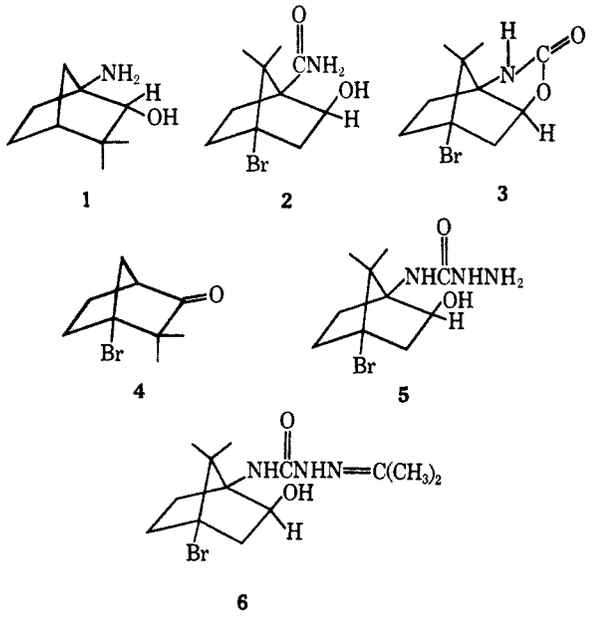
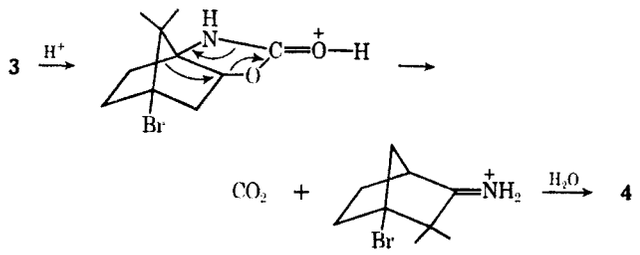


1 2 3 4 5 6

variation of a well-known Wagner–Meerwein rearrangement attended by decarboxylation and hydrolysis.

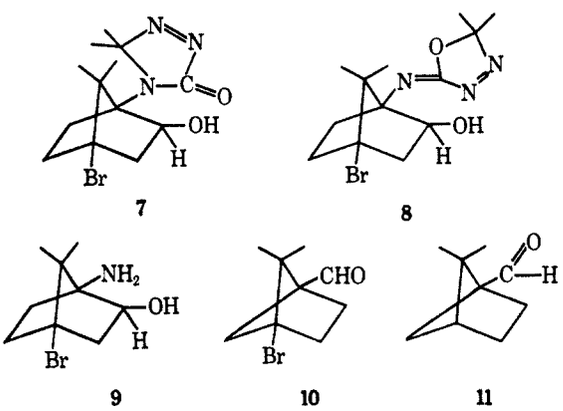
Other hydrolytic experiments with both acids and bases failed either because of lack of reaction or excessive destruction of the product. The N-nitroso derivative



of **3** could not be thermally degraded to identifiable products in contrast to N-alkyl-N-nitrosoamides.[15]

Hydrazine cleaved the heterocyclic ring of **3** effectively, and the semicarbazide **5** was converted into the semicarbazone **6**. Oxidation of **6** with lead tetraacetate did not produce the expected azoacetate.[16] The ir spectrum of the product showed absorption at 5.88 μ, and a singlet at δ 1.68 in the nmr spectrum was assigned to the *gem*-dimethyl group in the heterocyclic ring. Structure **7** is consistent with these data. The isomeric compound **8** may have been present, but **8** was not isolated. A recent report on the oxidation of semicarbazones with lead tetracetate relates that O to C cyclization occurs, *i.e.*, compounds of type **8** form.[17] Factors that determine which cyclization occurs, N to C (**7**) or O to C (**8**), are not known. The formation of the cyclic azo compound **7** is a new cyclization reaction which may be useful for the preparation of acylazo compounds.[18]

Hydrolysis of **7** was accomplished by 0.4 *N* hydrochloric acid at room temperature for 3 hr, and neutralization afforded the amino alcohol **9**. The transformations, **6** → **7** → **9**, need study on readily available compounds to attain optimum experimental conditions and also to determine the mechanisms of the reactions. The hydroxyl group of **9** is assumed to have the *exo* configuration which was assigned to 4-bromo-7,7-dimethyl-2-hydroxybicyclo[2.2.1]heptane-1-carbonitrile.[13]



7 8 9 10 11

Deamination of the amino alcohol **9** with nitrous acid furnished the aldehyde **10** from which the ir spectrum showed absorption bands at 3.57, 3.69, and 5.87 μ that characterize the carbonyl group. Bands at 7.22 and 7.28 μ indicated that the *gem*-dimethyl group was intact. Nmr spectroscopy facilitates the identification of bicyclo[2.1.1]hexane derivatives,[4,10,19,20] and the spectrum of **10** is consistent: δ 0.96 (singlet, 3 H, C-5 *endo*-CH_3), 1.32 (singlet, 3H, C-5 *exo*-CH_3), 1.73 (doublet, 1 H, J = 7.5 cps, C-6 *endo*-H), 2.06 (multiplet, 4 H, C-2 and C-3 H_2), 2.72 (double multiplets, 1 H, J = 7.5 cps, C-6 *exo*-H), and 9.58 (singlet, 1 H, C-1 CHO). The deshielding effect of the bromo group at the bridgehead position is evident in the chemical shifts of the C-6 protons. The analog **11** provides a comparison: δ 1.06 (C-6 *endo*-H) and 2.08 (C-6 *exo*-H).[11]

The aldehyde **10** was oxidized to the corresponding acid **12** with potassium permanganate. The nmr spectrum corroborates the structure of the acid, but the acid was not obtained free of an impurity that was an unsaturated acid in which bromine was not present. Identification of the unsaturated acid was incomplete. Dehydrohalogenation of 1-bromobicyclo[2.1.1]hexane was observed by Wiberg and Lowry,[21] and the destruction of the bicyclic rings ystem in **12** must follow a similar course.

Substitution at the bridgehead position of bicyclo[2.1.1]hexane derivatives does not occur by direct halogenation,[8,22] and other methods have been devised to attain these compounds.[21,23] It is noteworthy that the formation of **10** was not impaired by dehydrohaologenation, which was not observed, if it occurred at all. The deamination of **9** and **1** provides **10** and **11** in yields that are approximately 70%. The successful ring contractions must be due to the favorable stereochemistry that obtains in these rigid bicyclic amines.

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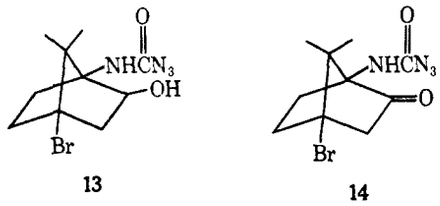
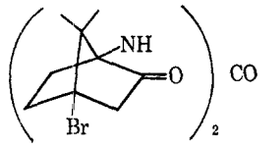
The configuration of the hydroxyl group at C-2 does not appear to be crucial.

Our initial experiments to convert the semicarbazide **5** into the amine **9** were not successful. The azide **13** was easily prepared, but reverted to **3** under hydrolytic conditions. Chromic acid oxidation of the azide provided **14**, and attempted decomposition of **14** yielded the urea **15** as the main product. Apparently the amine that formed reacted with the azide. The last reaction finds precedent in research by Carpino.[24]



13

14



15

Experimental Section

Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institute, Mülheim (Ruhr), Germany. Melting points were taken with total immersion theromometers. Nmr spectra were determined on a Varian A-60 instrument, and tetramethylsilane was used as the internal reference. The ir spectra were determined in KBr on a Beckman IR-5 spectrophotometer.

4-Bromo-7,7-dimethyl-2-hydroxybicyclo[2.2.1]heptane-1-carboxamide (2).—The amide was prepared from 4-bromo-7,7-dimethyl-2-hydroxybicyclo[2.2.1]heptane-1-carbonitrile according to the method of Noller.[25] The nitrile (4.40 g, 0.018 mol) was dissolved in 50 ml of ethanol. Hydrogen peroxide (50 ml of a 30% solution) and sodium hydroxide (7.7 ml of a 20% solution) were added. The solution was stirred efficiently at 30–50°, cooling when necessary, for 45 min. The solution was maintained at 50° for another 1.25 hr. Water (120 ml) was added, and the resulting mixture was cooled in ice. The product was isolated and recrystallized from ethanol. The amide amounted to 3.80 g (80% yield), mp 227–229° (lit.[12] mp 226–228°).

Anal. Calcd for $C_{10}H_{16}BrNO_2$: C, 45.80; H, 6.15; N, 5.34. Found: C, 45.78; H, 6.11; N, 5.26.

6-Bromo-5,6,7,7a-tetrahydro-8,8-dimethyl-4H-3a,6-methanobenzoxazolin-2-one (3).—The Hofmann reaction was done according to an established procedure.[26] A solution of sodium hydroxide (3.50 g, 0.0875 mol) in 30 ml of water was cooled to 0°. Sodium hypobromite was prepared by adding bromine (0.80 ml, *ca.* 0.015 mol) to the basic solution with stirring. The finely powdered amide **2** (3.01 g, 0.015 mol) was added to the hypobromite solution. The cold mixture was stirred until the amide dissolved (1–2 hr). The solution was warmed gently, not above 50°, for 5 min after the appearance of a white precipitate. The mixture was cooled and filtered. The product was washed with water and recrystallized from ethanol. Yields varied from 70 to 78% white crystals: mp 212–222° dec; λ_{max} 3.10 (broad, NH) and 5.75 μ (C=O).

Anal. Calcd for $C_{10}H_{14}BrNO_2$: C, 46.16; H, 5.42; Br, 30.71; N, 5.38. Found: C, 46.06; H, 5.45; Br, 30.74; N, 5.52.

The N-nitroso derivative of **3** was prepared according to a report by White.[27] The heterocycle **3** (1.0 g, 0.0038 mol) was dissolved in a mixture of acetic acid (4 ml) and acetic anhydride (19 ml). Sodium nitrite (5.91 g, 0.086 mol) was added in small amounts. The mixture was protected from light and was stirred for 1.5 hr. Water (150 ml) was added, and the precipitate was filtered. The dry product was crystallized from a mixture of ethyl acetate and hexane and amounted to 1.07 g (96%) of light yellow crystals: mp 188–194° dec; λ_{max} 5.49 (C=O) and 6.55 μ (N=O).

Anal. Calcd for $C_{10}H_{13}BrN_2O_3$: C, 41.53; H, 4.53; N, 9.69. Found: C, 41.18; H, 4.42; N, 9.63.

Thermal and alkaline treatment of the N-nitroso derivative led to products which we were unable to identify.

Hydrolysis of 3.—A solution of water (10 ml) and concentrated sulfuric acid (10 ml) was added to **3** (1.0 g), and the mixture was maintained at the reflux temperature for 30 min. The mixture was poured onto ice, and the solid was isolated and washed with water. The crude material amounted to 0.61 g (74%). Recrystallization of the product from hexane gave 1-bromo-2,2-dimethylbicyclo[2.2.1]heptan-3-one: mp 169.4–170.4°; λ_{max} 5.70 (C=O in five-membered ring), 7.22, and 7.33 μ (*gem*-dimethyl group); nmr ($CDCl_3$) δ 1.05 (singlet, 3 H), 1.14 (singlet, 3 H), and 1.33–2.70 (multiplets, 7 H).[28]

Anal. Calcd for $C_9H_{13}BrO$: C, 49.78; H, 6.03; Br, 36.81. Found: C, 49.85; H, 6.11; Br, 37.14.

Compound **3** was recovered from hot concentrated HCl. Treatment of **3** with 20% sodium hydroxide at the reflux temperature yielded a minute quantity of an acid, mp 93–96°. Additional study of the acid was not feasible.

4-(4-Bromo-2-hydroxy-7,7-dimethyl-1-norbornyl) Semicarbazide (5).—Compound **3** (8.0 g) was treated with 90% hydrazine (40 ml) at gentle reflux for 45 min. The cold mixture was diluted with 280 ml of water, cooled, and filtered. Recrystallization from ethanol provided 7.80 g (90%) of the semicarbazide **5**: mp 184–186° dec; λ_{max} 6.05 μ (C=O).

Anal. Calcd for $C_{10}H_{18}BrN_3O_2$: C, 41.09; H, 6.23; N, 14.37. Found: C, 41.09; H, 6.17; N, 14.42.

Acetone 4-(4-Bromo-2-hydroxy-7,7-dimethyl-1-norbornyl) Semicarbazone (6).—The semicarbazide **5** (18.0 g) was placed in acetone (115 ml), and the mixture was maintained at reflux for 2.5 hr. Some acetone was distilled, and the derivative crystallized. A yield of 18.4 g (90%) was obtained. Recrystallization from ethanol furnished crystals: mp 193–194°; λ_{max} 5.98 and 6.07 μ.

Anal. Calcd for $C_{13}H_{22}BrN_3O_2$: C, 46.98; H, 6.67; N, 12.64. Found: C, 46.90; H, 6.84; N, 12.62.

4-(4-Bromo-2-hydroxy-7,7-dimethyl-1-norbornyl)-5,5-dimethyl-Δ^1-1,2,4-triazolin-3-one (7).—An oxidation procedure by Iffland was used.[16] Lead tetraacetate (6.54 g, 0.015 mol) was placed in 50 ml of methylene chloride. The mixture was stirred at 0–10° while a solution of the semicarbazone **6** (4.70 g, 0.014 mol) in 200 ml of methylene chloride was added in a period of 15 min. The mixture was stirred for 20 min at room temperature, and water (200 ml) was added. The mixture was separated, and the organic phase was washed with water and sodium bicarbonate. After the solution was dried over anhydrous magnesium sulfate, the solvent was removed with a vacuum evaporator. The solid residue was recrystallized immediately from ethanol. The crystals amounted to 2.10 g (45%): mp 160–161°; λ_{max} 5.88 μ (C=O); nmr ($CDCl_3$) δ 1.68 (singlet, *gem*-dimethyl group in heterocyclic ring).

Anal. Calcd for $C_{13}H_{20}BrN_3O_2$: C, 47.26; H, 6.12; N, 12.72. Found: C, 47.16; H, 5.99; N, 12.69.

1-Amino-4-bromo-7,7-dimethylbicyclo[2.2.1]heptan-2-ol (9).—Compound **7** (0.30 g) was treated with dilute hydrochloric acid (5 ml) at room temperature for 2 hr. After filtration and neutralization with dilute sodium hydroxide, the precipitate was isolated by filtration. The crude product was obtained in a yield of 60%. Recrystallization from aqueous ethanol furnished crystals, mp 191–193° dec (bath preheated to 190°). The ir spectrum did not contain any absorption due to a carbonyl group.

Anal. Calcd for $C_9H_{16}BrNO$: C, 46.14; H, 6.91; N, 5.98. Found: C, 45.95; H, 6.90; N, 6.09.

It was convenient to hydrolyze the crude product from the lead tetraacetate oxidation immediately. After removal of the methylene chloride, the residue was treated with 200 ml of 0.40 *N* hydrochloric acid at room temperature for 3 hr. A magnetic stirrer was used. A gas was gradually evolved. Filtration was necessary before isolation of the product in the usual way. The over-all yields (**6** → **9**) were variable (38–59%).

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(25) C. R. Noller in "Organic Syntheses," Col. Vol. II, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 586.

(26) E. S. Wallis and J. F. Lane, *Org. Reactions*, **3**, 267 (1946).

(27) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6008 (1955).

(28) The nmr instrument was purchased through Grant GM 10413 from the U. S. Department of Health, Education, and Welfare.

4-Bromo-5,5-dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde (10).—The amino alcohol (1.21 g) was dissolved in 29 ml of a 50% acetic acid solution. The deamination was done under nitrogen at a temperature of 0–5°. A magnetic stirrer provided efficient stirring. Sodium nitrite (2.76 g, 0.04 mol) was dissolved in 10 g of water, and the solution was added in a period of 10 min. The cold mixture was stirred for an additional 20 min, and the acid was neutralized with a saturated solution of sodium carbonate. The solid product was isolated by filtration and washed with cold water. After the product was dried in a vacuum desiccator, sublimation [60–70° (1 mm)] furnished 0.75 g (66%) of aldehyde. Recrystallization from low-boiling petroleum ether (30–60°) afforded the aldehyde **10**: mp 125–127° (bath preheated to 120°); λ_{max} 3.57, 3.69, 5.87 (CHO group), 7.22, and 7.28 μ (*gem*-dimethyl group); nmr spectrum ($CDCl_3$) δ 0.96 (singlet, 3 H, C-5 *endo*-CH_3), 1.32 (singlet, 3 H, C-5 *exo*-CH_3), 1.73 (doublet, 1 H, J = 7.5 cps, C-6 *endo*-H), 2.06 (multiplet, 4 H, C-2 and C-3 H_2), 2.72 (double multiplets, 1 H, J = 7.5 cps, C-6 *exo*-H), and 9.58 (singlet, 1 H, C-1 CHO).

Anal. Calcd for $C_9H_{13}OBr$: C, 49.79; H, 6.04; Br, 36.81. Found: C, 49.67; H, 6.00; Br, 36.91.

The 4-toluenesulfonylhydrazone of aldehyde **10** was prepared. The aldehyde was transferred from the Hirsh funnel in the above procedure to a solution of 4-toluenesulfonylhydrazine (0.96 g) in the minimum amount of hot methanol. The derivative was prepared and isolated in the usual way. After recrystallization from methanol the hydrazone amounted to 1.44 g (72%), mp 133–134°.

Anal. Calcd for $C_{16}H_{21}BrN_2O_2S$: C, 49.87; H, 5.49; Br, 20.73. Found: C, 50.07; H, 5.49; Br, 20.99.

The semicarbazone was prepared from the aldehyde in the above procedure with the theoretical amount of semicarbazide hydrochloride and sodium acetate in aqueous ethanol. Recrystallization from ethanol furnished the derivative (45% yield) with mp 147–148° (bath preheated to 140°).

Anal. Calcd for $C_{10}H_{16}BrN_3O$: C, 43.79; H, 5.78; N, 15.32. Found: C, 43.80; H, 5.79; N, 15.50.

4-Bromo-5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylic Acid (12).—The aldehyde from the above preparation was dissolved in 50 ml of acetone and 4 ml of water. Powdered potassium permanganate (0.82 g) was added to the warm solution. Excess permanganate was destroyed with glycerol, and the solvent was removed. The residue was triturated several times with dilute base. After filtration, the alkaline solution was acidified. The solid product was isolated and sublimed at 60–80° (1 mm). The acid amounted to 0.51 g (42% based on **9**): mp 136–139°; nmr spectrum ($CDCl_3$) δ 0.95 (singlet, 3 H, C-5 *endo*-CH_3), 1.28 (singlet, 3 H, C-5 *exo*-CH_3), 1.80 (doublet, 1 H, J = 7.5 cps, C-6 *endo*-H), 2.07 (multiplet, 4 H, C-2 and C-3 H_2), 2.65 (double multiplets, 1 H, J = 7.5 cps, C-6 *exo*-H), 11.28 (singlet, 1 H, C-1 COOH).

In one oxidation the product was an acid that did not contain bromine on analysis. After crystallization from aqueous ethanol the impure acid melted at 158–159°, and unsaturation was evident in the ultraviolet (uv) spectrum.

4-Bromo-2-hydroxy-7,7-dimethyl-1-norbornylcarbamyl Azide (13).—The semicarbazide **5** (1.51 g) was dissolved in 20 ml of 90% acetic acid. Sodium nitrite (5.52 g) was dissolved in 20 ml of water, and the solution was added dropwise to the semicarbazide. The solution was stirred for 1 hr at room temperature. The product precipitated on the addition of water. The solid was recrystallized from ethanol to furnish the azide (70%): mp 151–152° dec; λ_{max} 4.66 (azide) and 5.95 μ (C=O).

Anal. Calcd for $C_{10}H_{15}BrN_4O_2$: C, 39.61; H, 4.98; N, 18.47. Found: C, 39.76; H, 4.84; N, 18.49.

4-Bromo-7,7-dimethyl-2-oxo-1-norbornylcarbamyl Azide (14).—The azide **13** (2.89 g) was added to glacial acetic acid (150 ml) that contained 0.95 g of chromium trioxide. The solution was stirred for 2 hr at room temperature. The solvent was neutralized with sodium carbonate, and the product was extracted with ether. The ethanol solution was dried with anhydrous magnesium sulfate, and the solvent was removed with a vacuum evaporator. Crystallization of the residue from aqueous ethanol gave the azide **14** (56% yield): mp 150–151°; λ_{max} 3.00 (NH), 4.67 (N_3), 5.72 (C=O), and 5.83 μ (C=O).

Anal. Calcd for $C_{10}H_{13}N_4O_2$: C, 39.87; H, 4.35; N, 18.59. Found: C, 40.23; H, 4.25; N, 18.10.

1,3-Di-4-bromo-7,7-dimethyl-2-oxo-1-norbornylurea (15).—The azide **14** (2.0 g) was dissolved in 30 ml of tetrahydrofuran. Dilute hydrochloric acid (10 ml) was added, and the solution was maintained at reflux for 1 hr. The acid was neutralized with dilute sodium hydroxide and the volatile solvent was removed with a vacuum evaporator. The residue was extracted with ether. The ethereal solution was dried and the solvent was removed. The residue was crystallized from ethyl acetate to provide the product **15** (25% yield): mp 228–230° dec; λ_{max} 3.0 (NH), 5.70 (C=O), and 5.93 μ (C=O).

Anal. Calcd for $C_{19}H_{26}BrN_2O_3$: C, 46.53; H, 5.34; N, 5.71. Found: C, 46.58; H, 5.61; N, 5.75.

Registry No.—**3**, 19029-14-2; **3** (N-nitroso derivative), 39029-15-3; **5**, 19029-16-4; **6**, 19029-17-5; **7**, 19029-18-6; **9**, 19029-19-7; **10**, 19029-51-7; **10** (4-toluenesulfonylhydrazone), 19039-29-3; **10** (semicarbazone), 19039-30-6; **12**, 19039-31-7; **13**, 19029-20-0; **14**, 19029-21-1; **15**, 19029-22-2; 1-bromo-2,2-dimethylbicyclo[2.2.1]heptan-3-one, 13743-41-4.

Free-Radical α Bromination of Cyclopropyl Compounds by N-Bromosuccinimide

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Received August 7, 1968

Attempts to carry out free-radical bromination of norcarane using N-bromosuccinimide (NBS) resulted solely in rearrangement of the NBS to β-bromopropionyl isocyanate. However, with the model systems cycloprop[2,3]indene, benzylcyclopropane, *trans*-1-benzyl-2-methylcyclopropane, and bicyclo[4.1.0]hept-3-ene, in which the carbons α to the cyclopropane rings are activated toward radical formation by adjacent phenyl or vinyl substituents, azobisisobutyronitrile-initiated NBS bromination in carbon tetrachloride solution proceeds smoothly and rapidly. Product formation in each case is derived predominantly *via* initial hydrogen atom abstraction from a carbon α to a cyclopropane ring. Bromide products derived both from cyclopropylcarbinyl and rearranged allylcarbinyl radical intermediates were observed. In certain cases, products resulting from ion-pair rearrangements and eliminations from initially formed, highly reactive cyclopropylcarbinyl bromides were also found.

During the past several years, considerable interest has been shown[1] in the chemistry of systems which can react *via* formation of cyclopropylcarbinyl or allylcarbinyl radical intermediates. Much of this work was done with the objective of finding evidence for rate accelerations caused by cyclopropyl or homoallyl participation at the transition states in radical-forming reactions. Also, information was sought regarding whether two discrete classical radical intermediates or a

(1) For articles which summarize much of the research which has been done in this area, see: (a) C. Walling in "Molecular Rearrangements," Vol. I, P. DeMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 407–455; (b) R. Breslow, ref 1a, pp 289–294; (c) L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Amer. Chem. Soc.*, **89**, 923 (1967); (d) S. J. Cristol and R. V. Barbour, *ibid.*, **90**, 2832 (1968).