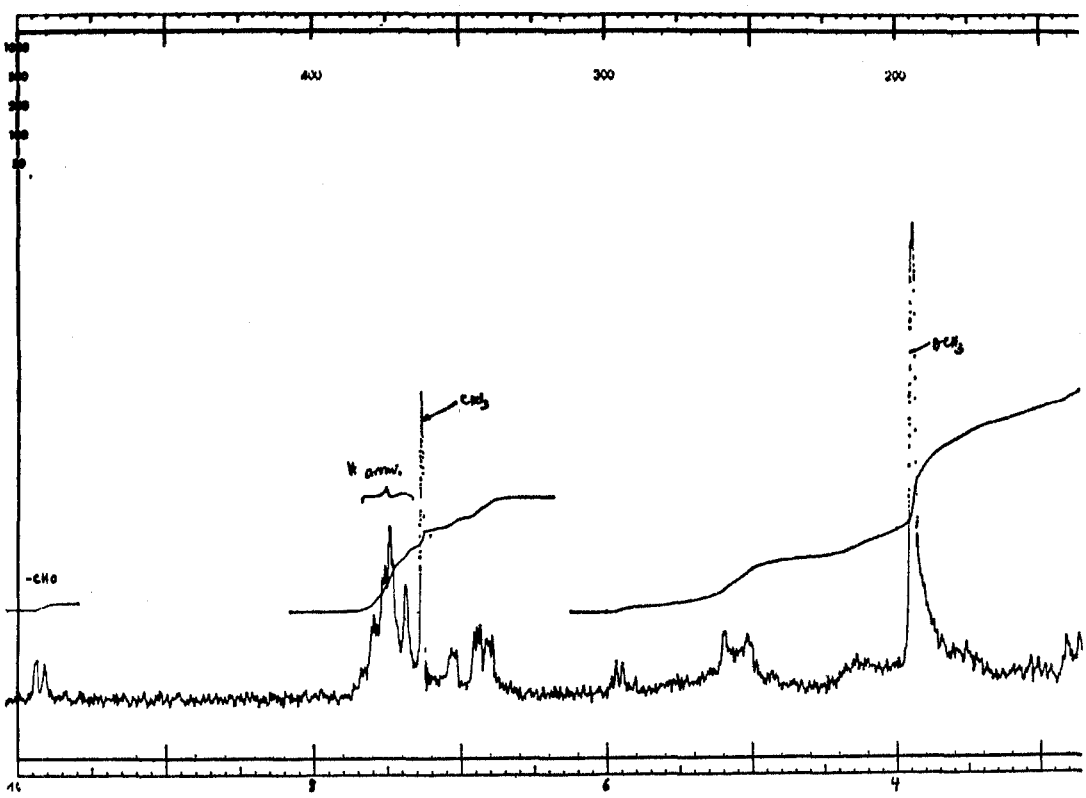
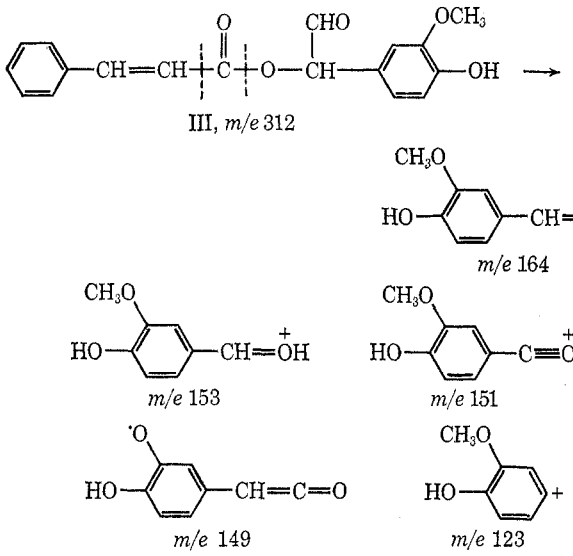


Figure 4.—Nmr spectrum of component B.

cps). These evidences together with the mass spectral fragmentation pattern (Scheme II), significant peaks at *m/e* 164, 153, 151, 149, and 123, indicate structure III for B.

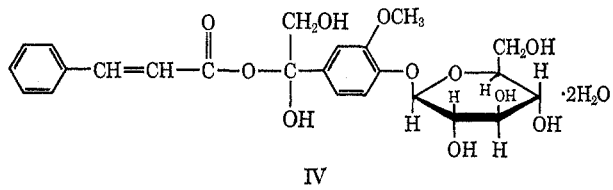
SCHEME II

MASS SPECTRAL FRAGMENTATION PATTERN OF B



See Figures 1–3 for infrared spectra of A, B, and kutkin. Figure 4 shows the nmr spectrum of B.

On the basis of structures II and III for the two major degradation products, we propose the following revised structure IV for the glucoside, kutkin. The physical data (nmr[9] and ir spectra, high optical rotation,[2] and analyses, *loc. cit.*) are consistent with the structure IV for kutkin. The observed hydrolysis of kutkin with emulsin indicates its β-glucosidic linkage.



IV

Registry No.—IV, 25356-80-3.

Acknowledgment.—K. B. is grateful to the Ministry of Health, Government of India, for the award of a Research Fellowship. Financial assistance from the ICMR (CDRS), New Delhi, is thankfully acknowledged.

(9) Dr. U. Scheidegger, Varian AG Research Laboratory, Switzerland, also opined, on the basis of nmr data, for the above structural assignments of kutkin and its two major degradation products, for which the authors are indebted.

Synthesis of 2-(2-Nitroalkyl)benzoates[1]

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Received December 19, 1969

Methyl 2-(2-nitroethyl)benzoate (**4**) was required for a synthesis[2] of 2-nitroindanone. A possible approach seemed to be selective hydrogenation of methyl 2-(2-nitrovinyl)benzoate (**3**). The latter compound was thought to be accessible by applying the β-nitro-

(1) Taken from the Ph.D. Thesis of S. R. Naik, University of Ottawa, 1967.

(2) H. H. Baer and S. R. Naik, *J. Org. Chem.*, **35**, 2927 1970.

SCHEME I

styrene synthesis[3] to methyl phthalaldehydate (**1**), provided that, for the nitromethane condensation, conditions not affecting the ester grouping were found.[4] Examining a variety of conditions, we obtained the hitherto unknown products **6**, **8**, **9**, and **10**, but **3** could not be isolated.

When the reaction was performed in refluxing acetic acid in the presence of ammonium acetate,[5] the lactam **6** was isolated in poor yield. Presumably it arose by way of amination of intermediate **3** followed by internal aminolysis (**1** → **2** → **3** → **5** → **6**). Substitution of sodium acetate for ammonium acetate, as well as triethylamine-catalyzed reaction in methanolic solution at room temperature, led to a compound $C_{17}H_{11}NO_6$ which exhibited infrared and ultraviolet absorptions very similar to those reported for the known[4,6] 3-phthalidylnitromethane (**7**). The product was therefore formulated as bis(3-phthalidyl)nitromethane (**8**). It obviously arose by combination of two molecules of **1** with one molecule of nitromethane, with lactone formation from intermediate hydroxy esters, in the sequences **1** → **2** → **7** → **8** or **1** → **2** → **8**. Performance of the reaction at 0° using nitromethane as the solvent and benzyltrimethylammonium hydroxide as the catalyst gave 2-(1,3-dinitro-2-propyl)benzoic acid (**9**) which yielded the methyl ester (**10**) by the action of diazomethane. The formation of **9** may be envisioned as proceeding *via* **2** and **7**. The latter compound is known[4] to undergo lactone opening by β elimination induced by strong base, and in the presence of excess nitromethane this process is evidently accompanied by a Michael addition leading to the dinitro acid. See Scheme I.

Attempts at synthesizing **3** from **1** and nitromethane, with sodium methoxide, sodium hydrogen carbonate, dimethylamine, piperidine, or pyridine as the catalyst and methanol or benzene as the solvent, resulted in the recovery of starting material and (or) the formation of unidentifiable products. The sodium bisulfite procedure[7] also failed. Therefore, an alternate route to **4** was elaborated.

2-(2-Bromoethyl)benzoic acid (**11**), obtained from isochroman-1-one[8] by fission with hydrogen bromide,[8b] was converted into its (liquid) methyl ester (**12**) by diazomethane. It was observed that distillation of **12** requires carefully controlled conditions as this ester tends to suffer thermal cleavage, thereby reverting to isochroman-1-one.[9] Treatment of **12** with sodium nitrite in dimethyl sulfoxide[10] gave the nitro ester **4** in about 60% yield. The bromo acid (**11**) was converted into its phenyl ester (**13**) *via* the acid chloride, and

(3) B. Priebs, *Ber.*, **16**, 2591 (1883); *Justus Liebigs Ann. Chem.*, **225**, 319 (1884). J. Thiele, *Ber.*, **32**, 1293 (1899). H. Knoevenagel, *ibid.*, **37**, 4502 (1904). F. W. Hoover and H. B. Hass, *J. Org. Chem.*, **12**, 501 (1947). V. V. Perekalin, "Unsaturated Nitro Compounds," translated by L. Mandel, Israel Service of Scientific Translations, Ltd., Jerusalem, 1964.

(4) It was known that the free acids corresponding to intermediate **2** and to **3** spontaneously cyclize to 3-phthalidylnitromethane (**7**); see H. H. Baer and F. Kienzle, *Can. J. Chem.*, **43**, 190 (1965).

(5) C. B. Gairaud and G. R. Lappin, *J. Org. Chem.*, **18**, 1 (1953). S. Byrdy, Z. Eckstein, and J. Plenkiewicz, *Bull. Acad. Pol. Sci., Sér. Sci. Chim.*, **9**, 627 (1961). See also M. G. S. Rao, C. Srikantia, and M. S. Iyengar, *Helv. Chim. Acta*, **12**, 581 (1929).

(6) T. Széki, *Ber. Ung. Pharm. Ges.*, **13**, 680 (1937); *Chem. Abstr.*, **31**, 6644 (1937). B. B. Dey and T. K. Srinivasan, *Arch. Pharm. (Weinheim)*, **275**, 397 (1937). G. E. Ullyot, J. J. Stehle, C. L. Zirkle, R. L. Shriner, and F. J. Wolf, *J. Org. Chem.*, **10**, 429 (1945). H. H. Baer and B. Achmatowicz, *ibid.*, **29**, 3180 (1964).

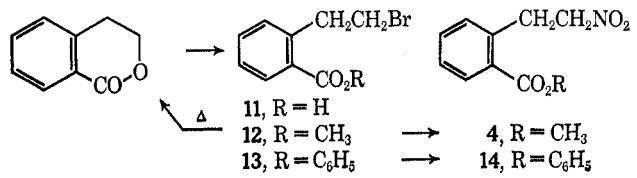
(7) J. Kamlet, U. S. Patent No.2,151,517 (1939); *Chem. Abstr.*, **33**, 5003 (1939).

(8) (a) J. Cologne and P. Boisde, in "Les Hétérocycles Oxygénés," Centre National de la Recherche Scientifique, Paris, 1957, p 177; (b) P. Maitte, *ibid.*, p 197.

(9) Possibly this is caused by attack of the carbonyl oxygen on the bromo carbon atom, resulting in displacement of bromide ion and formation of a resonance-stabilized cyclic oxonium salt which collapses to isochromanone and methyl bromide.

(10) N. Kornblum, *Org. React.*, **12**, 101 (1962).

treatment of **13** with sodium nitrite produced a crystalline substance that appeared to be a mixture of the expected nitro ester **14** and starting **13**. Pure **14** was separated by preparative thin layer chromatography. The cyclization of **4** and **14** to 2-nitroindanone is disclosed elsewhere.[2]



Experimental Section[11]

Methyl Phthalaldehydate (1).[12]—A solution of commercial phthalaldehydic acid (15.0 g, 0.1 mol) in warm water (100 ml) was cooled to room temperature, and a solution of potassium carbonate (6.91 g, 0.05 mol) in water (15 ml) was added gradually. A small amount of insoluble matter was filtered off, and to the heated (70°) and vigorously stirred filtrate was added a hot solution of silver nitrate (17.88 g, 0.105 mol) in water (25 ml). The mixture was allowed to cool in the dark, and the white silver phthalaldehydate was filtered off, washed thoroughly with water, and then with ethanol. After drying at 80° the salt was suspended in ether (200 ml) containing methyl iodide (21.4 g) and refluxed for 2 hr. The insoluble matter was filtered off and washed with ether, and the filtrate was dried (Na_2SO_4) and evaporated to leave a pale yellow oil. Distillation at 13 Torr gave 12.9 g (78.6%) of colorless **1** collected at 136–138° [lit.[12,13] bp 136–138° (13 mm), bp 146–147° (17 mm)]. Strong ir bands were at 1720 (ester C=O), and 1695 cm^{-1} (aldehyde C=O); a weak band at 1770 cm^{-1} (α,β-unsaturated γ-lactone) indicated a small degree of contamination by the pseudo ester, 3-methoxyphthalide.

2-(1-Amino-2-nitroethyl)benzolactam (6).—A mixture of **1** (0.75 g), nitromethane (0.75 ml), ammonium acetate (0.3 g), and glacial acetic acid (3 ml) was refluxed for 2 hr. The pale yellow liquid was cooled and poured onto crushed ice. The product was extracted with chloroform (25 ml) which was washed twice with water, dried (Na_2SO_4), and evaporated. By trituration of the semisolid residue with ethyl acetate (2 ml), crude **6** (102 mg) melting at 175–185° could be isolated. Recrystallization from ethyl acetate gave colorless needles (78 mg), mp 193°, ν_{max} 3225 (NH), 1720 (amide I),[14] and 1550 cm^{-1} (NO_2).

Anal. Calcd for $C_9H_8N_2O_3$ (192.1): C, 56.25; H, 4.16; N, 14.57. Found: C, 56.22; H, 3.94; N, 14.82; OCH_3, 0.0.

Bis(3-phthalidyl)nitromethane (8). A. Catalysis by Sodium Acetate.—A mixture of **1** (0.75 g), nitromethane (0.75 ml), anhydrous sodium acetate (0.3 g), and glacial acetic acid (3 ml) was refluxed for 2 hr and then evaporated to dryness. The yellow residue was extracted with dry benzene and the extract concentrated to a small volume. Addition of a few drops of petroleum ether induced slow crystallization of colorless **8** (75 mg) that melted at 175–190° (at 226° after recrystallization from acetonitrile). Ir and uv spectra were identical with those of **8** described in section B.

B. By Catalysis with Trimethylamine.—A solution of **1** (4.92 g, 0.03 mol) and nitromethane (2.80 g, 0.046 mol) in methanol (50 ml) was chilled in an ice–water bath, and 5% methanolic trimethylamine (30 ml) was added dropwise, with stirring, in the course of 30 min. Stirring was continued for 5 hr at room temperature, and after renewed cooling to 0° the mixture was neutralized with cold 1 *N* HCl to about pH 4. Most of the methanol was then removed by evaporation, and the remaining, largely aqueous solution was extracted with ether (100 ml). The ethereal extract was washed twice with water, dried (Na_2SO_4), and evaporated to leave a yellow oil which was distilled at 20 Torr. A fraction collected at 150–151° weighed 3.6 g and was identified as starting ester **1** (recovery, 73%). The residue of distillation was treated with benzene (2 ml) and a few drops of petroleum ether, which caused colorless crystals (250 mg) of impure **8** (mp 175–185°) to be deposited within a few hours. Recrystallization from acetonitrile gave 125 mg of prisms: mp 230°, ν_{max} 1760 (C=O) and 1560 cm^{-1} (NO_2); λ_{max} 276 nm (ϵ 5300) and 283 (5200) in methanol.

Anal. Calcd for $C_{17}H_{11}NO_5$ (325.2): C, 62.77; H, 3.38; N, 4.30. Found: C, 62.88; H, 3.28; N, 4.41; mol wt, 325 (mass spectrum).

2-(1,3-Dinitro-2-propyl)benzoic Acid (9).—A solution of **1** (2.46 g, 0.015 mol) in nitromethane (12.5 g, 0.2 mol) was added dropwise (over a period of 2 hr) to a stirred and chilled (0 to −3°) solution of benzyltrimethylammonium hydroxide (6 ml, 40% in methanol, technical grade) in nitromethane (18.3 g, 0.3 mol). When the addition was complete the mixture was allowed to stand for another 15 min at 0° and was then neutralized with chilled 1 *N* HCl and extracted with ether (100 ml). The extract was washed twice with water, dried over Na_2SO_4, and evaporated to give a pale yellow, semisolid residue from which a crystalline material (2.15 g, mp 125–127°) could be isolated by trituration with benzene (5 ml). Two recrystallizations from benzene afforded colorless needles (1.0 g, plus 0.25 g from the mother liquors): mp 138–139°; ν_{max} 3300–3100 and 2700–2400 (OH), 1680 (C=O), and 1560 with shoulder at 1550 cm^{-1} (NO_2); nmr data (in acetone-d_6) τ 2.5–3.1 (m, 4 H, aromatic), 5.20 (m, 1 H, benzylic), 5.50 (d, 4 H, $2CH_2NO_2$). In the mass spectrum, the molecular ion peak expected at *m/e* 254 was not observed, but a fragment with *m/e* 208 was present (loss of NO_2).

Anal. Calcd for $C_{10}H_{10}N_2O_6$ (254.2): C, 47.22; H, 3.94; N, 11.03. Found: C, 47.44; H, 4.09; N, 10.82.

Methyl 2-(1,3-Dinitro-2-propyl)benzoate (10).—An ethereal solution of diazomethane was added in slight excess to the acid **9** (610 mg) in ether (50 ml). After 1 hr the solvent was evaporated and the residue was recrystallized from methanol to give colorless plates (462 mg, 72%) of **10**: mp 90°; ν_{max} 1720 (C=O) and 1570 with shoulder at 1560 cm^{-1} (NO_2); nmr data ($CDCl_3$) τ 1.9–2.6 (m, 4 H, aromatic), 4.78 (m, 1 H, benzylic), 5.08 (d, 4 H, 2 CH_2NO_2), 6.10 (s, 3 H, CO_2CH_3). In the mass spectrum, the molecular ion peak expected at *m/e* 268 was not observed, but a fragment with *m/e* 237 was present (loss of OCH_3).

Anal. Calcd for $C_{11}H_{12}N_2O_6$ (268.2): C, 49.26; H, 4.51; N, 10.44. Found: C, 49.49; H, 4.70; N, 10.50.

Isochroman-1-one.—This compound was prepared[8] by selenium dioxide oxidation of commercial isochromane: nmr data (CCl_4) τ 2.05 (m, 1 H) and 2.65 (m, 3 H), aryl protons, 5.58 and 7.70, two sharp, symmetrical triplets (2 H each) with spacings of 6 Hz (A_2X_2 pattern of CH_2CH_2). No impurities were revealed. Characteristic ir bands (from liquid film) are given for comparison with **12**: 1720 s, 1610 m, 1460 m, 1427 w, 1390 m, 1293 s, 1240 s, 1121 s, 1103 m, 1090 s, 1063 m, 1035–1030 s, 992 w, 954 m, 805 m, 748 s, 716 w, 696 s, 640 m.

2-(2-Bromoethyl)benzoic Acid (11).—Commercial 30% hydrogen bromide in acetic acid was saturated by passing through dry hydrogen bromide gas at 0°. Isochromanone (10 g) was introduced into 40 ml of the reagent, and the mixture was heated in a sealed tube for 3 hr at 150°. After cooling to room temperature the tube was chilled in Dry Ice before opening. Removal of the reagent *in vacuo* led to a residue that crystallized from carbon tetrachloride. The yield of **11** was 11.7 g, mp 93° (lit.[8b] mp 93.5°): nmr data ($CDCl_3$) τ 1.75 (m, 1 H) and 2.45 (m, 3 H), aryl protons, 6.32 (narrow multiplet, 4 H), bromoethyl group. No trace of isochromanone was present.

Methyl 2-(2-Bromoethyl)benzoate (12).—The acid **11** (3.0 g) in ether (75 ml) was treated with a slight excess of ethereal diazomethane for 1 hr. Upon removal of the solvent **12** was obtained as pale yellow oil that was dried *in vacuo*: ir data (from liquid film) 1720 s, 1600 m, 1575 m, 1485 m, 1448 s, 1433 s, 1290 s, 1270 s, 1255 s, 1215 m, 1185 m, 1115 s, 1075 s, 1050 w, 1030 w, 965 m, 755 s, 715 s, 650 m; nmr data (CCl_4) τ 2.0 (m, 1 H) and 2.6 (m, 3 H), aryl protons, 6.11 (s, 3 H), CO_2CH_3, 6.45 (m, 4 H), bromoethyl group. No signals attributable to impurities were seen.

(11) All evaporations were performed *in vacuo* at about 40°. Melting points were taken in capillaries in an electric aluminum block apparatus. Infrared spectra were obtained, from Nujol mulls unless otherwise stated, with a Perkin-Elmer Infracord or a Beckman IR-8 instrument, and only the most characteristic bands are given. Nmr spectra (60 MHz) were recorded on a Varian HA-60 spectrometer and were internally standardized with tetramethylsilane.

(12) K. v. Auwers and A. Heinze, *Ber.*, **52**, 595 (1919), wherein few experimental details were recorded. Other methods of esterification of phthalaldehydic acid were stated to give 3-methoxyphthalide.

(13) E. L. Eliel and A. W. Burgstahler, *J. Amer. Chem. Soc.*, **71**, 2251 (1949).

(14) In dilute solution in chloroform the carbonyl band was at 1710 cm^{-1}, close to that reported (1698 cm^{-1}) for phthalimidine; see A. E. Kellie, D. G. O'Sullivan, and P. W. Sadler, *J. Chem. Soc.*, 3809 (1956).

Anal. Calcd for $C_{10}H_{11}BrO_2$ (243.1): OCH_3, 12.75. Found: OCH_3, 12.50.

When a sample of **12** was distilled from a short-neck bulb at 0.3 Torr and 95–100° (bath temperature), the distillate gave unchanged ir and nmr spectra. Distillation of a larger quantity of **12** from an ordinary flask at 0.8 Torr and 108–110° (bath, 140–160°) caused the distillate to contain a considerable amount of isochromanone as revealed by spectroscopy. After three such distillations a sample was found to be nearly free from bromine (Found: Br, 0.42. Calcd for **12**: Br, 32.87.) and to give C and H values corresponding to isochromanone (Found: C, 73.34; H, 5.90. Calcd: C, 72.97; H, 5.40.).

Phenyl 2-(2-Bromoethyl)benzoate (13).—The acid **11** (508 mg) was refluxed with thionyl chloride (2 ml) for 1 hr. The excess of the reagent was then distilled off, and the reaction product was dissolved in pyridine (5 ml). Phenol (209 mg) was added, and the mixture was magnetically stirred for 2 hr at ambient temperature. The crystalline precipitate was discarded and the solution was evaporated to dryness. Crystallization of the residue from ethanol afforded colorless, hexagonal plates (400 mg) of the phenyl ester, mp 84°, ν_{max} 1730 cm^{-1}.

Anal. Calcd for $C_{15}H_{13}BrO_2$ (305.2): C, 59.00; H, 4.29; Br, 26.17. Found: C, 59.23; H, 4.16; Br, 26.06.

Methyl 2-(2-Nitroethyl)benzoate (4).—The bromo ester **12** (710 mg), sodium nitrite (350 mg), and phloroglucinol (166 mg) were stirred in dimethyl sulfoxide (3 ml) at room temperature for 8 hr. The mixture was then triturated with crushed ice, and the solid precipitate was collected and dried (375 mg, mp 45–48°). Recrystallization from methanol afforded **4** as colorless rods, mp 55–56°, ν_{max} 1720 (C=O) and 1550 cm^{-1} (NO_2).

Anal. Calcd for $C_{10}H_{11}NO_4$ (209.2): C, 57.41; H, 5.29; N, 6.69. Found: C, 57.20; H, 4.99; N, 6.35.

Use of sodium nitrite in *N,N*-dimethylformamide or of silver nitrite in ether failed to afford **4**.

Phenyl 2-(2-Nitroethyl)benzoate (14).—The bromo ester **13** (305 mg) and sodium nitrite (110 mg) were stirred in dimethyl sulfoxide (5 ml) at room temperature for 4 hr. The mixture was poured into ice water which was immediately extracted with three portions of ether. Thecom bined extracts were washed twice with water, dried (Na_2SO_4), and evaporated to give a colorless solid (155 mg). Recrystallization from ethanol furnished prisms, mp 71°, ν_{max} 1730 (C=O) and 1550 cm^{-1} (NO_2). This material showed two major spots in tlc on silica gel G with cyclohexane–chloroform (2:3, v/v). The nitrogen content (2.47%) was half of that expected, and the carbon content (63.35%) lay between the values calculated for **14** and **13**. Separation of the mixture by preparative tlc furnished unreacted **13** (77 mg) by chloroform extraction of the faster moving band, and pure **14** (60 mg, mp 81°) by extraction of the slow moving band.

Anal. Calcd for $C_{15}H_{13}NO_4$ (271.3): C, 66.40; H, 4.83; N, 5.16. Found: C, 66.20; H, 4.86; N, 5.33.

Extension of the reaction time to 24 hr yielded a product that was difficult to purify.

Registry No.—**4**, 25109-81-3; **6**, 25109-82-4; **8**, 25109-83-5; **9**, 25109-84-6; **10**, 25109-85-7; **12**, 25109-86-8; **13**, 25109-87-9; **14**, 25158-13-8.

Acknowledgment.—Support of this work by the National Research Council of Canada is gratefully acknowledged.

Synthesis of Bridgehead Functionalized Bicyclo[3.3.1]nonanes

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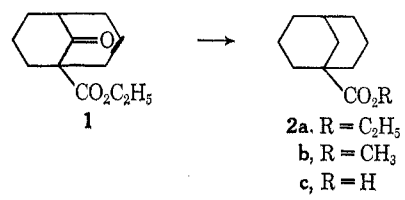
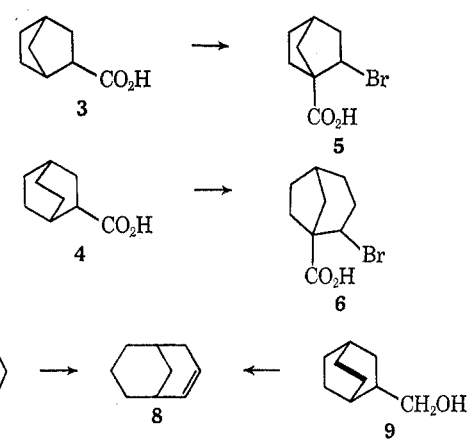
A wide variety of synthetic routes to the bicyclo[3.3.1]nonane ring system involves annelation of a three-membered bridge to the α positions of a cyclohexanone derivative.[1] Some of these methods[1c-f] have been applied to the synthesis of bicyclononanes functionalized at the bridgehead,[2] and our previous synthesis[3] of 1-ethoxycarbonylbicyclo[3.3.1]nonane (**2a**) is typical, being based on previous work. As we desired a compound functionalized only at the bridgehead, the ester **1** (prepared from acrolein and 2-ethoxycarbonylcyclohexanone[1c,d]) was converted to the ethylene dithioketal which was desulfurized with Raney nickel to give the ester **2a**. While the yields for this procedure are satisfactory, the desulfurization step is cumbersome and somewhat dangerous because of the quantities of Raney nickel which must be handled on large runs. Thus we have sought an alternative method for the synthesis of **2**.



1

2a, R = C_2H_5
b, R = CH_3
c, R = H

Our alternative synthesis is based on the reports that bicyclo[2.2.1]heptane-2-carboxylic acid[4] (**3**) and bicyclo[2.2.2]octane-2-carboxylic acid[5] (**4**) rearrange when brominated under Hell–Volhard–Zelinsky conditions to give acids **5** and **6**, respectively. Hartmann[6] has shown



3 **5** **4** **6** **7** **8** **9**

(1) For example, see (a) V. Prelog, P. Barman, and M. Zimmermann, *Helv. Chim. Acta*, **32**, 1284 (1949); (b) V. Prelog, P. Barman, and M. Zimmermann, *ibid.*, **33**, 356 (1950); (c) A. C. Cope and M. E. Synerholm, *J. Amer. Chem. Soc.*, **72**, 5228 (1950); (d) E. W. Colvin and W. Parker, *J. Chem. Soc.*, 5764 (1956); (e) R. P. Nelson and R. G. Lawton, *J. Org. Chem.*, **34**, 1225 (1969); (f) S. Danishevsky, G. Koppel, and R. Levine, *Tetrahedron Lett.*, 2257 (1968); (g) P. W. Hickmott and J. R. Hargraeves, *Tetrahedron*, **23**, 3151 (1967); (h) G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.*, **78**, 5130 (1956); (i) A. C. Cope, D. L. Nealy, P. Scheiner, and G. Wood, *ibid.*, **87**, 3130 (1965).

(2) For other routes to bridgehead-substituted bicyclononanes, see (a) W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968); (b) P. von R. Schleyer and P. R. Isele, *ibid.*, **33**, 1239 (1968); (c) J. P. Ferris and N. C. Miller, *J. Amer. Chem. Soc.*, **85**, 1325 (1963); (d) H. Meerwein and W. Schurmann, *Justus Liebigs Ann. Chem.*, **398**, 196 (1913); (e) R. Rabe and M. Jahr, *ibid.*, **360**, 276 (1908).

(3) (a) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, **92**, 956 (1970); (b) J. R. Wiseman, *ibid.*, **89**, 5966 (1967).

(4) (a) W. R. Boehme, *ibid.*, **81**, 2762 (1959); (b) H. Kwart and G. Null, *ibid.*, **81**, 2765 (1959).

(5) A. W. Chow, D. R. Jakas, and J. R. E. Hoover, *Tetrahedron Lett.*, 5427 (1966).

(6) M. Hartmann, *Z. Chem.*, **7**, 101 (1967).