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Synthesis and Polymerization Studies of Bicyclo[2.1.0]pentene-1-carbonitrile and Bicyclo[3.1.0]hexane-1-carbonitrile

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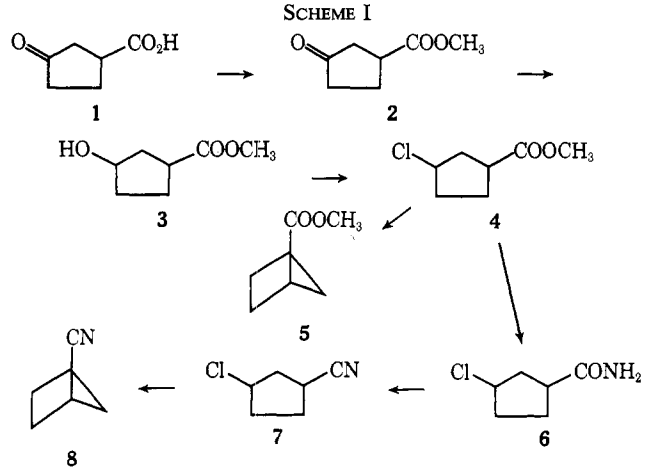
ABSTRACT: Bicyclo[2.1.0]pentane-1-carbonitrile and methyl bicyclo[2.1.0]pentane-1-carboxylate were synthesized by base-induced ring closure from the corresponding 3-chlorocyclopentanes. They did not polymerize or copolymerize by free-radical initiation, but did undergo anionic polymerization. Bicyclo[3.1.0]hexane-1-carbonitrile was synthesized *via* ring closure of a 1,3-disubstituted cyclohexane derivative; it did not polymerize.

Previous articles of this series[2,3] described the synthesis and polymerization of various bicyclobutanes, of which bicyclobutane-1-carbonitrile and methyl bicyclobutane-1-carboxylate were of most interest. Release of strain constituted the driving force for these polymerizations involving opening of a C–C single bond. It was of interest to extend this novel polymerization to other strained bicyclic nitriles.

Bicyclo[2.1.0]pentanes. This ring system contains the second most strained C–C single bond,[4] and was our first choice. 3-Cyclopentanonecarboxylic acid (**1**) was prepared by minor modification of literature procedures.[5] Esterification and hydrogenation gave the hydroxy ester **3** which with thionyl chloride in dimethylformamide gave methyl 3-chlorocyclopentanecarboxylate (**4**). From this compound, the best syntheses were those shown in Scheme I. Ring closure

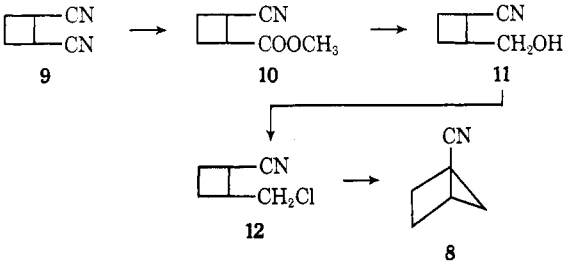
SCHEME I



to the bicyclic ester **5**, uncontaminated by olefin, was effected by sodium hydride in *N*-methylpyrrolidone in 72% yield. Ester **5** has been prepared previously by photolysis of pyrazolines.[6–8] The nitrile **8** was less easily prepared. Sodium amide in refluxing tetrahydrofuran gave the best yield, 37%. These are the first syntheses of bicyclo[2.1.0]pentanes from 1,3-disubstituted cyclopentanes.

A second synthesis (Scheme II) resembled that independently worked out for *n*-butyl bicyclo[2.1.0]pentane-1-carboxylate by Gassman and Mansfield.[6] Lithium borohydride was used

SCHEME II



in the reduction step; the chlorination was accomplished by triphenylphosphine in carbon tetrachloride.[9] Thionyl chloride did not react, although it readily converts the corresponding 2-cyanocyclopropanemethanol to the chloride. Sodium amide in tetrahydrofuran cyclized this in low yield to bicyclo[2.1.0]pentane-1-carbonitrile (**8**), identical with the previous sample. This behavior contrasts with that of 2-chloromethylcyclopropanecarbonitrile,[2] which did not give 1-bicyclobutanecarbonitrile under these conditions.

Bicyclo[3.1.0]hexanes. Bicyclo[3.1.0]hexane-1-carboxamide (**13**) was prepared according to Nelson and Mortimer[10] and converted to the corresponding nitrile **14**.

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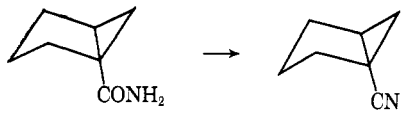
(10) N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957).



13 14

Polymerizations. Methyl bicyclopentane-1-carboxylate and bicyclo[2.1.0]pentane-1-carbonitrile did not undergo free radical homo- or copolymerizations but anionic polymerizations did proceed. Butyllithium in tetrahydrofuran gave a low polymer from the ester and gave a high yield of polymer, mp ~250°, η_{inh} 0.5 from the nitrile. No polymers were obtained on similar treatment of bicyclo[3.1.0]hexane-1-carbonitrile.

Conclusions. A bridgehead ester and nitrile of bicyclo[2.1.0]pentane were prepared. Despite greater ring strain, they did not undergo radical polymerization as do the corresponding bicyclobutanes. More vigorous anionic reagents do give polymers. Bicyclo[3.1.0]hexane-1-carbonitrile did not give either radical or anionic polymers. Thus, as the size of the bridge fused to cyclopropane increases from one to two to three methylenes, ease of polymerization decreases sharply.

Experimental Section

Bicyclo[2.1.0]pentane Series. 3-Cyclopentanonecarboxylic Acid (1). The following procedure is an improvement of literature procedures, chiefly in that undistilled intermediates are used throughout to avoid decomposition. A 5-l., four-necked flask was fitted with a motor driven stirrer, reflux condenser, nitrogen "T," and a 1-l. relieved dropping funnel. The flask was dried with a heat gun with a nitrogen sweep. In it was placed 134 g of a 54% dispersion of sodium hydride in mineral oil. The oil was removed from the sodium hydride by washing twice with 750-ml portions of stock pentane and removal of the solvent with a filter stick. The clean sodium hydride was covered with 900 ml of stock tetrahydrofuran. With ice cooling a mixture of 475 g of dimethyl itaconate (Pfizer Co.) and 791 g of dimethyl malonate was added with stirring. The reaction is exothermic at beginning of the addition and a pot temperature of between 20 and 30° was maintained by selective addition. The reaction was stirred overnight at room temperature. The pot contents were poured into a mixture of 300 ml of 12 *N* HCl and 750 ml of ice and water. It was stirred vigorously for 30 min during which time color changed to yellow. The water layer was separated and washed twice with 250-ml portions of chloroform. The combined organic layers were back-washed with 250 ml of saturated KCl solution, dried, and concentrated on a rotary evaporator at aspirator pressure at 35°. Excess dimethyl malonate, bp 55° (200 μ), was distilled keeping pot temperature below 105°.

The crude tetramethyl butanetetracarboxylate was mixed with 167.5 g of commercial sodium methoxide and 1.84 l. of toluene in a round-bottomed flask with a Vigreux head. It was heated to an inner temperature of 91–100°. After 1 hr, about 400 ml of liquid, bp 70–80°, distilled. The cooled pot contents were added to a mixture of 360 ml of 12 *N* HCl and 1500 ml of ice and water. The mixture was stirred vigorously for 30 min. The water layer was separated and extracted three times with 370 ml of chloroform. The combined organic layers were back-washed with 610 ml of saturated KCl, dried, concentrated on a rotary evaporator at 35° and aspirator pressure, and finally evacuated at 0.5 mm for at least 1 hr. The crude yield of dimethyl cyclopentanonedicarboxylate was about 650 g.

The diester was mixed in a 5-l., three-necked flask with a solution of 225 ml of 96% sulfuric acid in 3.6 l. of distilled water. The mixture was heated to reflux with motor stirring, and methanol and water were distilled in such a manner that after 500 ml of distillate was removed, 500 ml of distilled water was added to the flask. This process was repeated until at least 2 l. was removed and added. The pot contents were filtered and the precipitate (usually a very small amount) was washed with about 10 ml of water. The filtrate was continuously extracted with ether for 4 days. The extract was concentrated on the rotary evaporator at 35° and aspirator pressure. It could be distilled directly to give, after some gassing (decarboxylation), 140–160 g of crude acid which when redistilled yielded 125–140 g (32–36% overall yield) of pure crystalline 3-cyclopentanecarboxylic acid (**1**). However, for avoidance of decomposition, it was better to esterify the crude acid directly, nmr τ 0.90 (s, 1, CO_2H), 6.79 (m, 1), 7.41 (s, 1), 7.67 (m, 5).

Methyl 3-Cyclopentanonecarboxylate (2). A mixture of crude 3-cyclopentanonecarboxylic acid (389.0 g, ~3.11 mol), 2,2-dimethoxypropane (478 ml), methanol (81 ml), and methanesulfonic acid (3.0 g) was stirred at 62° for 21 hr under reflux. The mixture was cooled, concentrated on the rotary evaporator, then diluted with 3 l. of ether. With ice cooling, ammonia was bubbled into the solution causing immediate precipitate formation. When the precipitate formation ended, the ammonia was stopped and the mixture filtered. The ether layer was evaporated and distilled through a Vigreux column to yield, after a small forerun, 221.3 g (50.1%) of methyl 3-cyclopentanonecarboxylate (**2**), bp 64–69° (0.5 mm), 48° (0.25 mm) (lit.[5] bp 69° (14 mm)).

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.62, 59.35; H, 7.45, 7.48.

Ir showed OCH_3 7.13 μ (m), 5.74 (s), ester C=O, CH 3.38 μ (s, sh); nmr τ 6.34 (s, 27, OCH_3), 6.88 (m, 1.4), 7.79 (m, 5.9, spike at 7.59).

Methyl 3-Hydroxycyclopentanecarboxylate (3). Hydrogenation of methyl 3-cyclopentanonecarboxylate to methyl 3-hydroxycyclopentanecarboxylate over PtO on charcoal at 50° without a solvent proceeded smoothly. The nmr spectrum was useful in determining completeness of hydrogenation, showing a spike for unreacted keto ester at τ 7.58 in $CDCl_3$, while the hydroxy ester is transparent there. Product **3** boiled at 57° (0.1 mm) (lit.[5] bp 106° (15 mm)); ir 5.76 μ (s, ester C=O), CH 3.36 μ (s), OH 2.93 μ (s); nmr τ 6.36 (s, 3, OCH_3), 7.20 (m, 1), 8.10 (m, 5.9), 5.70 (m, 1, CHOH), 6.05 (s, 1, OH) (transparent at 7.59).

Methyl 3-Chlorocyclopentanecarboxylate (4). Thionyl chloride, 750.0 g (6.30 mol), was added over a 1.5-hr period to an ice–CH_3OH-chilled solution of methyl 3-hydroxycyclopentanecarboxylate, 860 g (5.96 mol), and 15 ml of DMF. The temperature increased from 0 to 20° during the addition of $SOCl_2$. The solution was held at 63° for 0.5 hr, cooled, and poured into excess water. The solution was extracted with ether (8 lb in several batches), washed with KCl solution and H_2O, and dried. Distillation gave 681.9 g of crude product, bp 75–95° (15 mm), which was combined with 335.3 g of crude product from an earlier experiment. The combined products were distilled through a helix-packed column to yield 109.3 g, bp 43–95° (17 mm), of forerun which consisted mainly of dimethylformamide and a cyclopentanecarboxylate. The main fraction was 747.5 g (51.9%) **4**, bp 90–99° (17 mm). Starting material, 32 g, was recovered.

Anal. Calcd for $C_7H_{11}O_2Cl$: C, 51.70; H, 6.82. Found: C, 51.96, 51.93; H, 7.31, 6.93.

Gc analysis showed 63% of one isomer and 31% of the other, combined purity 95%; ir CH 3.40 (s, sh), 5.74 (s), and 5.79 (s) μ, ester C=O, OCH_3 8.3–8.7 μ (s); nmr τ 6.34 (s, 3, OCH_3), 7.86 (m, 7), 5.55 (m, 1, CHCl).

Methyl Bicyclo[2.1.0]pentane-1-carboxylate (5). Sodium hydride dispersion, 45 g (1.0 mol) of a 54% dispersion in mineral oil, was cleaned with two 200-ml portions of pentane. The sodium hydride was covered with 675 ml of redistilled *N*-methylpyrrolidone and to the mixture was added with stirring a solution of 145.6 g (0.895 mol) of methyl 3-chlorocyclopentanecarboxylate in 100 ml of *N*-methylpyrrolidone. The reaction mixture was maintained at 45° with water cooling during the addition, which required 35 min. Hydrogen, 20.3 l., was evolved. The reaction mixture was stirred for an additional 1.5 hr and was cooled to 0°. To it were added 675 ml of ether and 675 ml of saturated ammonium chloride solution. The layers were shaken well and separated. The aqueous layer was extracted four times with 900 ml of ether. The organic layers were back-washed with 420 ml of saturated potassium chloride solution, dried, and evaporated. Distillation through a spinning band column gave 81.6 g (72.2%) of methyl bicyclo[2.1.0]pentane-1-carboxylate (**5**), bp 50° (10 mm) (lit.[6] bp 78° (43 mm)). The com-

pound was 98.8% pure by gas chromatography and the nmr spectrum was transparent in the vinyl region.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99; mol wt, 126.2. Found: C, 66.46; H, 7.71; mol wt, 126 (mass spectrum).

Ir 5.81 μ (s, ester C=O), 3.27 (m), 3.35 (s), 3.40 (s), and 3.48 (s); nmr τ 6.40 (s, 3, OCH_3), 8.28 (m, 7, CH).

Anionic Oligomerization of Methyl Bicyclo[2.1.0]pentane-1-carboxylate. Treatment of the ester, 1 ml, with 0.1 ml of diethylmagnesium slurry in 4 ml of toluene at −35° overnight led in work-up to a little viscous oil whose spectrum was satisfactory for the corresponding polymer, ir sat. CH 3.38 μ (m) and 3.47 (w), C=O 5.75 μ (m).

3-Chlorocyclopentanecarboxamide (6). In each of five separate runs 3-chlorocyclopentanecarboxylate (149.4 g) and 880 ml of NH_4OH were stirred vigorously for 48 hr. The mixture was filtered and the liquid filtrate was concentrated on the rotary evaporator and azeotropically dried with toluene. The precipitate was then added to the mixture and the azeotropic drying with toluene repeated. Each residue obtained was dissolved in 0.8 l. of EtOAc, filtered hot, chilled, filtered, and pumped dry to give 464.7 g (crop no. 1) from five runs. The filtrates of all five runs were combined, evaporated, and recrystallized from ~300 ml of ethyl acetate to give 106.2 g (crop no. 2) of product. The total yield was 570.9 g (84.2%) of 3-chlorocyclopentanecarboxamide. Crop 1 melted at 149.0–151.6°.

Anal. Calcd for C_6H_9OClN: C, 48.82; H, 6.83. Found: C, 48.83, 48.88; H, 6.94, 6.85.

Ir showed $CONH_2$ 2.99 μ (s) and 3.14 (s), CH 3.35 μ (m) and 3.56 (w), amide C=O, 6.05 (s, broad), $CONH_2$ 6.1 (s, broad); nmr τ 3.07 (broad d, 1.8, $CONH_2$), 5.49 (m, 0.9, CHCl), 8.07 (m, 7.3).

3-Chlorocyclopentanecarbonitrile (7). 3-Chlorocyclopentanecarboxamide, 46.7 g (0.32 mol), and P_2O_5 (93.4 g, 0.66 mol) were mixed thoroughly and distilled in a Claisen head apparatus. A flame was used as the heat source and the pressure was ~15 mm, gradually lowered to 10 mm and finally 0.5 mm. Distillation was continued until only a black residue was left. The yield was 25.48 g (63%), bp 98–103° (~10 mm), 43° (0.1 mm), of 3-chlorocyclopentanecarbonitrile which darkened upon standing. Redistillation of the crude product, 430 g, from 827.7 g (5.61 mol) (converted in 50-g batches) in a spinning band column gave 19.1 g, bp 28–29° (0.8–1.1 mm), of forerun; a small (~8 g) intermediate cut, bp 44–53.5°, consisting of cyclopentenenitriles, which was discarded; a main cut of 265.5 g of **7**, bp 52–52.5° (0.5 mm), which was a single isomer; and 65.0 g of **7**, bp 58–85° (0.35–0.20 mm), a mixture of two isomers. The total yield was 350.5 g (46.5%).

Anal. Calcd for C_6H_8NCl: C, 55.60; H, 6.24; N, 10.81; Cl, 27.35. Found: C, 55.77, 56.10; H, 6.50, 6.68; Cl, 27.15.

Ir showed C≡N 4.45 μ (m), CH 3.37 (m), 8.69 (w), 10.55 (m), 11.10 (m); nmr τ 5.56 (m, 0.96, CHCl), 7.79 (m, 7.04).

Bicyclo[2.1.0]pentane-1-carbonitrile (8) *via* **3-Chlorocyclopentanecarbonitrile.** 3-Chlorocyclopentanecarbonitrile, 26.0 g (0.2 mol), was dripped into sodium amide (prepared under argon from 6.9 g (0.3 mol) of Na and 425 ml of liquid NH_3 followed by addition of 400 ml of THF and distillation of ammonia). The reaction was followed by gas chromatography. After 3.0 hr the reaction was shown to be over so the mixture was cooled and NH_4Cl added with stirring. The THF layer was separated. The salt sludge was washed well with THF. The organic layers were washed with saturated KCl solution, dried over $MgSO_4$, and evaporated on the rotary evaporator. The crude product was distilled to give 10.9 g (58.5%) of **8**, bp 48–50° (1 mm). Gc examination of the product showed 98.1% purity. Infrared and 100-Mc nmr spectra also supported the assigned structure. The latter clearly separated the absorptions into clumps containing 3, 1, and 3 H's.

Anal. Calcd for C_6H_7N: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.60, 77.60; H, 7.86, 7.85; N, 15.45, 15.22.

Ir showed CH 3.25 μ (w), 3.34 (w), 3.38 (m), and 3.47 (w), CN 4.48 (m); nmr τ 8.10 (m).

Some preparations contained traces of olefinic impurities. These could be removed by treatment with cold aqueous neutral permanganate, followed by decolorization with SO_2, extraction with dichloromethane, and distillation.

Bicyclo[2.1.0]pentane-1-carboxamide (15) and -carboxylic Acid (16). A mixture of the ester **5**, 81.6 g (0.647 mol), with 283 ml of concentrated ammonium hydroxide was stirred for 7 days at room temperature. It was chilled and filtered to give after drying 11.1 g of white crystals. The filtrate was concentrated on a rotary evaporator to leave a sticky white solid. This was extracted with 800 ml of boiling ethyl acetate and then with 500 ml of the same. The first extract, after concentration, gave 9.2 g of white crystals and the second gave 1.33 g. The combined yield of bicyclo[2.1.0]pentane-1-carboxamide (**15**) was 30.0%. After crystallization from ethyl acetate, it melted at 160–163°.

Anal. Calcd for C_6H_9ON: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.06, 63.93; H, 8.38, 8.29; N, 12.97, 13.07.

Ir showed $CONH_2$ 3.01 μ (m) and 3.16 (m), CH 3.36 (w), 3.42 (m), and 3.49 (w), amide C=O 6.03 (s), $CONH_2$ 6.19 (s); nmr τ 4.01 (m, 1.6, $CONH_2$), 8.08 (m, 7.4).

Distillation under vacuum from P_2O_5 gave bicyclo[2.1.0]pentane-1-carbonitrile (**8**) in 7% yield.

A small amount of bicyclo[2.1.0]pentane-1-carboxylic acid (**16**) could be obtained from the sticky solid above by dissolving it in water, acidifying, and extracting. Acid **16**, 0.65 g (1%), boiled at 61–65° (0.2 mm).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.27; H, 7.21.

Ir showed CH 3.27 μ (w), 3.34 (w), 3.39 (m), and 3.49 (w), OH 3.5–4 (m, broad), C=O 5.95 (s); nmr τ −2.47 (s, 1, CO_2H), 8.23 (m, 7).

Methyl 2-Cyanocyclobutanecarboxylate (10). To a mixture of 205.7 g (1.94 mol) of cyclobutane-1,2-dicarbonitrile (**9**) and 186 g (5.80 mol) of methanol was added with stirring 558 g (5.81 mol) of methanesulfonic acid. Ice cooling maintained the temperature at 25°. Then heating was begun cautiously. When the inner temperature reached 70°, an exothermic reaction began and the heating mantle was replaced by an ice–water bath. After heat evolution ceased, the reaction was maintained at 70° for 20 hr and cooled. It was diluted with 3 l. of ether and, with ice cooling, gaseous ammonia was passed in. When excess ammonia had been added, the precipitate salts were filtered and washed well with ether. The ether filtrate was concentrated and distilled, bp 52° (0.6 mm), −80° (0.2 mm). Redistillation in a 67 × 1.7 cm helix-filled column gave (i) a mixture of diester and methyl methanesulfonate, bp 34–50° (0.15 mm), 135.7 g; (ii) methyl methanesulfonate, bp 53.0–54.5° (0.15 mm), 39.52 g, nmr 6.12 (s, 3, OCH_3) and 6.99 (s, 3, CH_3SO_2); (iii) a mixture with methyl 2-cyanocyclobutanecarboxylate, bp 56.0–58.5° (0.15 mm), 44–65 g; and (iv) methyl 2-cyanocyclobutanecarboxylate (**10**), bp 58.5–60.5° (0.15 mm), 72.6 g (26.9%). The gc trace was that of a single isomer, but a very small afterrun showed a small amount of another peak.

Anal. Calcd for $C_7H_9O_2N$: C, 60.42; H, 6.52. Found: C, 60.50, 60.69, 60.75; H, 7.10, 6.70, 6.72.

Ir showed CH 3.31 μ (m), 3.36 (s), and 3.45 (w); C≡N 4.44 μ (m), C=O 5.74 μ (s); nmr ($CDCl_3$–D_2O, slow exchange) τ 6.24 (s) and 6.29 (s, total 3, OCH_3), 6.61 (m, 2, α-H), 7.71 (m, 4, ring).

2-Hydroxymethylcyclobutanecarbonitrile (11). Methyl 2-cyanocyclobutanecarboxylate, 28.0 g (0.202 mol), was added over a 5-min period to an ice-cooled, N_2-swept solution of $LiBH_4$, 4.4 g (0.20 mol), in 150 ml of isopropyl alcohol. The mixture was stirred for 0.5 hr in an ice bath and then for 1.0 hr without the bath, during which time the temperature rose to 48°. After stirring another 2.0 hr, the mixture was rotary evaporatored three times with toluene. The crude product was stirred overnight in 10 ml of H_2O and 500 ml of ether, then another 0.75 hr after $MgSO_4$ had been added. The solution was evaporated and distilled (bath 120–130°, 0.9 mm), from which 19.0 g (84.6%) of **11** was obtained. An analytical sample of **11** was distilled (with some loss due to decomposition) through a spinning band column, 8.05 g, bp 96° (0.6 mm).

Anal. Calcd for C_6H_9ON: C, 64.84; H, 8.16; N, 12.60. Found: C, 65.06, 65.08; H, 7.98, 8.08; N, 12.31, 12.26.

Ir showed OH 2.95 μ (s), CH 3.41 (m), CH 3.50 (m), C≡N 4.49 (m); nmr τ 6.30 (s) and 6.44 (s, total 3, CH_2OH), 7.11 (m, 1.9, α-H), 7.94 (m, 4.2, ring).

2-Chloromethylcyclobutanecarbonitrile (12). A mixture of 200 ml

of carbon tetrachloride, triphenylphosphine (56.9 g, 0.217 mol), and crude 2-hydroxymethylcyclobutanecarbonitrile (25.47 g, 0.229 mol) was stirred at 25° for 4.6 hr. A heavy white solid was obtained by evaporation of the reaction mixture. The solid was diluted with 0.75 l. of pentane, filtered through Celite, evaporated, and distilled. Distillation gave a small forerun, bp 35–87° (8 mm), plus the purified product **12**, bp 90–91° (7 mm), in a 33.2% yield. Use of pure starting material led to a 78% yield of the same product.

Anal. Calcd for C_6H_8NCl: C, 55.60; H, 6.25; Cl, 27.36. Found: C, 56.26, 56.56; H, 6.44, 6.38; Cl, 26.59.

Ir showed CH 3.37 μ (m), CH 3.46 (w), C≡N 4.45 (m); nmr τ 6.40 (m, 2.1, CH_2Cl), 7.02 (m, 2.1, α-H), 7.86 (m, 4.2, ring).

Bicyclo[2.1.0]pentane-1-carbonitrile (8) *via* **2-Chloromethylcyclobutanecarbonitrile.** 2-Chloromethylcyclobutanecarbonitrile (4.0 g, 0.031 mol) was added all at once to a refluxing solution of sodium amide (made from 1.0 g (0.043 mol) of Na in the usual way) in 125 ml of THF. After 20 min, gc showed the reaction to be ~10% completed. Another gc sample, taken after 1.75 hr, showed no starting material left. The mixture was chilled, 2 hr after reaction started, in an ice bath, and aqueous NH_4Cl was added. The THF layer was decanted and the remaining solid was washed with THF. The combined organic layers were washed twice with KCl, dried, and evaporated to a semisolid residue. This was taken up in 100 ml of pentane, triturated, filtered, evaporated, and distilled to yield 0.4 g (13.9%) of bicyclo[2.1.0]pentane-1-carbonitrile (**8**), bp 53° (9 mm). The infrared spectra showed no C=C to be present and was identical with that of the same compound made from 3-chlorocyclopentanecarbonitrile.

Anionic Polymerization of Bicyclo[2.1.0]pentane-1-carbonitrile. The following polymerizations were performed (monomer, solvent, and initiator, respectively, are given in parentheses): 1 (1 ml, 2 ml of THF, 0.2 ml of *n*-BuLi), 2 (1 ml, 2 ml of toluene, 0.2 ml of Et_2Mg), 3 (0.3 ml, 2 ml of THF, 0.05 ml of CH_3Li).

In each case the initiator was added at −80°, maintained by liquid nitrogen–ethanol. A bright green carbanion formed immediately in each case. The mixtures were held for several hours at −80, −35, 0, and 28°. Polymerization occurred quickly and completely at the intermediate temperatures. The reactions were worked up by blending twice with methanol, filtering, and drying to give >80% yields of white powder. On the hot bar, melting points of 240–254 and 228–240° to form clear pale brown melts were noted. After drying in an Abderhalden pistol over P_2O_5 they were analyzed.

Anal. Calcd for $(C_6H_7N)_x$: N, 15.04. Found: N (Dumas), 14.75, 14.59.

Ir showed C≡N 4.49 μ (m), CH 3.38 (m), and 3.47 (m); η_{inh} (DMF, 0.1%) 0.50.

Bicyclo[3.1.0]hexane-1-carbonitrile (14). To a suspension of 8.0 g (0.064 mol) of bicyclo[3.1.0]hexane-1-carboxamide (**13**)[10] and 5.41 g (0.064 mol) of pyridine in 22 ml of boiling chloroform was added during 18 min a solution of 8.1 g (0.068 mol) of thionyl chloride in 22 ml of chloroform. The mixture was then stirred and refluxed for 1 hr and cooled. It was washed with 1.1 ml of concentrated hydrochloric acid in 42 ml of water, with 2.12 g of sodium hydroxide in 42 ml of water, and with 4.2 ml of saturated potassium chloride solution in 21 ml of water. Each extract was back-washed with chloroform. The combined organic extracts were dried and evaporated. The residue was diluted with pentane and chilled. Unreacted amide (0.87 g) was filtered. The filtrate was distilled to give 4.53 g (66.9%) of bicyclo[3.1.0]hexane-1-carbonitrile (**14**), bp 61–63° (10 mm).

Anal. Calcd for C_7H_9N: C, 78.46; H, 8.47. Found: C, 77.61, 77.53; H, 8.18, 8.16.

The compound was 99.3% pure by gas chromatography: ir (CH) 3.38 (m) and 3.46 (m), (CN) 4.48 (m); nmr τ 8.28 (m).

Polymerization Attempts. An attempt to copolymerize, by an emulsion recipe, 1 ml of acrylonitrile with 1 ml of bicyclo[3.1.0]-hexane-1-carbonitrile gave 0.8 g (~100%) of polyacrylonitrile, η_{inh} (DMF) 0.75. The bicyclic does not copolymerize or interfere. With sodium hydride in tetramethylene sulfoxide no polymer formed. With ethylene, no cycloadduct formed, but polyethylene containing a trace of N was isolated. Heating the nitrile alone with azobisisobutyronitrile gave no polymer.

Synthesis and Polymerization of 2-Oxabicyclo[2.1.1]hexan-3-ones (Cyclobutane 1,3-Lactones)

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ABSTRACT: Five new 1,3-bridged cyclobutane lactones (2-oxabicyclo[2.1.1]hexan-3-ones) were synthesized. They polymerized readily with acidic or basic initiators to high molecular weight polyesters.

Ring opening polymerizations of a variety of bridged bicyclic lactones have been described.[2] The present work deals with the synthesis and polymerization of several 1,3-bridged cyclobutane lactones (2-oxabicyclo[2.1.1]hexan-3-ones).

Synthesis of Monomers. The lactones were prepared in each case from the corresponding 3-chlorocyclobutanecarboxylic acid. *cis,trans*-3-Chlorocyclobutanecarboxylic acid was available beginning with the cycloaddition of allene to acrylonitrile.[3] Addition of hydrogen chloride to 3-methylenecyclobutanecarboxylic acid gave *cis,trans*-3-chloro-3-methylcyclobutanecarboxylic acid; the same compound could be prepared from 3-methylenecyclobutanecarbonitrile by heating with concentrated hydrochloric acid. Completely analogous sequences of reactions starting from methacrylonitrile or α-trifluoromethylacrylonitrile led to the corresponding 3-chloro acids carrying a methyl or an α-trifluoromethyl group at the 1 position.

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