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)

H. K. Hall, Jr.,*[1] E. P. Blanchard, Jr., and E. L. Martin

Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware 19898.

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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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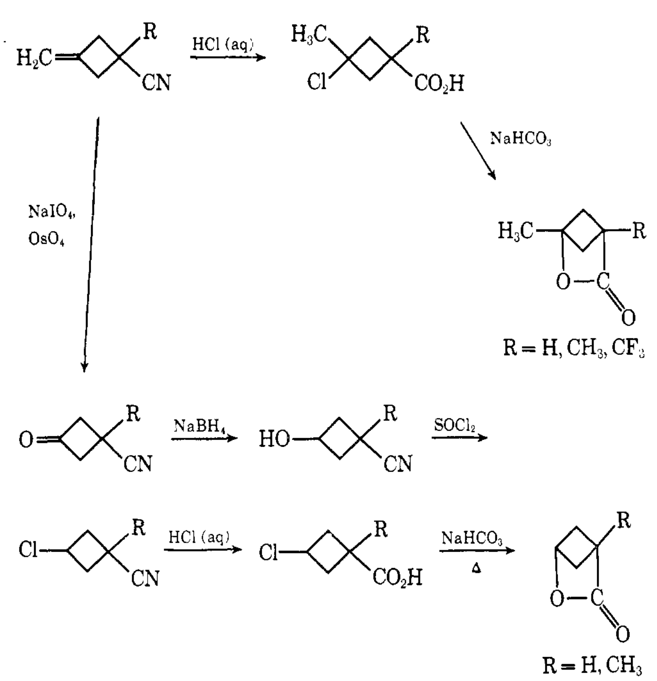
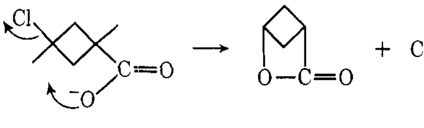
(1) Address correspondence to this author at the Department of Chemistry, University of Arizona, Tucson, Ariz. 85721.

(2) H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **80**, 6412 (1958).

(3) H. K. Hall, Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Sieja, and W. A. Sheppard, *ibid.*, **93**, 110 (1971).



Sodium or potassium salts of the 3-chlorocyclobutanecarboxylic acids cyclized on heating to give lactones *via* internal nucleophilic displacements, *e.g.*



In each case only one isomer, presumably trans, of the cis, trans chloro acids cyclized.

Polymerization. The new monomers polymerized readily when heated with a variety of basic or acidic initiators. High molecular weight, rather high-melting polyesters were obtained and could be melt pressed or cast into films or spun into fibers. They were soluble in acidic solvents such as trifluoracetic acid and in halogenated solvents such as chloroform.

We conclude that the 2-oxabicyclo[2.1.1]hexan-3-ones are a strained group of lactones resembling β-lactones rather than γ-lactones in their ability to polymerize. Up to two substituents on the ring do not decrease the tendency to polymerize, again like the β-lactones.

Triphenylmethylsodium. A procedure for making triphenylmethylsodium from sodium dispersion is given in the Experimental Section.

Experimental Section

2-Oxabicyclo[2.1.1]hexan-3-one. A mixture of 78.3 g (0.58 mol) of 3-chlorocyclobutanecarboxylic acid,[3] 97.5 g (1.16 mol) of sodium bicarbonate, and 0.35 l. of dibutyl phthalate was placed in a 2-l., three-necked flask fitted with a Nester–Faust motor-driven stirrer and a distillation head connected to condenser, receiver, and vacuum pump. With vigorous stirring and under full pump vacuum (0.5 mm), the mixture was brought to 110° using an oil bath at 130°. Pressure increased to ~10 mm, accompanied by vigorous frothing as the sodium salt formed. The mixture was held at this temperature until the pressure returned to 0.5 mm (~1 hr). The outer temperature was increased to 190° (inner 150°) and the lactone distilled slowly into the chilled receiver. When dibutyl phthalate began to reflux in the head, the experiment was terminated. The crude distillate was diluted with benzene, dried over magnesium sulfate, and concentrated on a rotary evaporator to a pale yellow liquid. Distillation in a 24-in. helix-packed column gave 2-oxabicyclo[2.1.1]hexan-3-one, 16.3 g (28.5%), bp 66.0–69.5° (5.5 mm).

Anal. Calcd for $C_5H_6O_2$: C, 61.21; H, 6.17. Found: C, 61.22; H, 5.93.

Ir showed 3.29 (m), 3.35 (m), 3.45 (w), CH, 5.55 (s), γ-lactone C=O; nmr τ 5.08 and 5.21 (doublet, with peaks split 1 Hz, 1, OCH), 7.08 (m, 1, HCC=O), 7.53 (m, 4, ring).

Final purification of the lactone for polymerization was accomplished by crystallizing it several times from ether at −80° and redistilling.

1-Methyl-3-methylenecyclobutanecarbonitrile. Cycloaddition of allene to methacrylonitrile at 200° for 8 hr was carried out as described[4] except that benzene was used as diluent. The product, bp 59° (26 mm), was pure by gc after distillation in a spinning band column.

3-Oxo-1-methylcyclobutanecarbonitrile. To a stirred slurry of 211.3 g (1.97 mol) of 3-methylene-1-methylcyclobutanecarbonitrile and 0.5 g of osmic acid in 2.46 l. of water at 0° was added in portions during 3 hr 890 g (4.16 mol) of sodium metaperiodate. The cooling bath was packed with fresh ice and the mixture stirred overnight as it gradually rose to room temperature. The heavy precipitate of sodium iodate was filtered and rinsed well with chloroform. The water layers were continuously extracted overnight with chloroform. The combined chloroform layers were dried and concentrated on a rotary evaporator. Two such runs gave 435 g of crude liquid. Distillation in a molecular still and redistillation in a spinning band column gave 295.1 g (68.2%) of product, bp 56° (0.5 mm).

Anal. Calcd for C_6H_7ON: C, 66.03; H, 6.47; N, 12.84. Found: C, 66.30; H, 6.79; N, 13.00.

Ir showed 3.34 (m), 3.39 (m), CH, 4.44 (m), CN, 5.55 (s), cyclobutanone C=O; nmr ($CDCl_3$) τ 8.31 (s, 3, CH_3), 6.16, 6.46, 6.75, 7.03 (wssw, further split, 4, ring).

1-Methyl-3-hydroxycyclobutanecarbonitrile. To a solution of 5.16 g (0.136 mol) of sodium borohydride in 230 ml of water at 35° was added 45.5 g (0.417 mol) of 3-oxo-1-methylcyclobutanecarbonitrile during 22 min with stirring. The reaction was mildly exothermic. The clear solution was stirred at room temperature for 2 hr and was extracted continuously for 24 hr with chloroform. Distillation through a Claisen head gave 44.5 g (96.0%) of 1-methyl-3-hydroxycyclobutanecarbonitrile, bp 68.5–75.0° (0.4 mm). The compound was neutral in water. The analytical sample was redistilled in a spinning band column.

Anal. Calcd for C_6H_9ON: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.78, 64.68; H, 8.13, 8.09; N, 12.40, 12.52.

Ir showed 3.34 (s) and 3.40 (s), CH, 2.94 (m) and 9.39 (s), OH, 4.46 (m), CN; nmr ($CDCl_3$ + D_2O) 5.76 (m, 1, OCH), 7.54 (m, 4, ring), 8.48 (s) and 8.53 (s), total 3 H, CH_3.

1-Methyl-3-chlorocyclobutanecarbonitrile. To thionyl chloride (159 g, 1.34 mol) was added at 55° with stirring a solution of dimethylformamide, 5 ml, in 111.0 g (1.0 mol) of 3-hydroxy-1-methylcyclobutanecarbonitrile over a 45-min period. During the addition the reaction temperature was kept at 55–57° with an oil bath. After an additional 1.0 hr at 55–57° the reaction mixture was cooled, concentrated on a rotary evaporator, and distilled through a Claisen head to yield 111.0 g (85.6%) of 1-methyl-3-chlorocyclobutanecarbonitrile, bp 38° (1.6 mm) to 42° (1.4 mm).

Anal. Calcd for C_6H_8NCl: N, 10.81; Cl, 27.35; Found: N, 10.33; 10.39; Cl, 26.73.

Ir showed 3.34 (m), 3.38 (m), and 3.47 (w), CH, 4.46 (m), CN; nmr τ 5.53 (1 H, m, α to Cl), 7.24 (4 H, m with two spikes, ring), 8.42 and 8.51 (3 H total, two singlets, CH_3); gc (silicone gum nitrile, 180°), two peaks only, ratio ~1:2.

3-Chloro-1-methylcyclobutanecarboxylic Acid. A mixture of 1-methyl-3-chlorocyclobutanecarbonitrile (109.0 g, 0.84 mol) and concentrated hydrochloric acid (0.8 l.) was stirred at reflux temperature for 20 hr and cooled to room temperature. The addition of chloroform (1.0 l.) dissolved all of the solid matter. The aqueous layer was extracted again with 1 l. of chloroform. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated on a rotary evaporator. Distillation in a molecular

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(4) H. N. Cripps, J. R. Williams, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **81**, 2723 (1959).

still gave 108.4 g (86.9%) of 3-chloro-1-methylcyclobutanecarboxylic acid, bp 114–117° (3.0 mm), which solidified to a white solid, mp 43.0–43.5°.

Anal. Calcd for $C_6H_9O_2Cl$: C, 48.50; H, 6.11. Found: C, 48.97, 48.73; H, 6.27, 6.26.

Ir showed broad, 3.35 (m), CH, jagged, 3.5–4 (m), COOH, 5.84 (s), carboxylic acid C=O; nmr τ 1.59 (1 H, s, CO_2H), 5.59 (1 H, m, HCCl), 7.39 (4 H, m, ring), 8.51 and 8.58 (3 H, two total singlets, CH_3).

4-Methyl-2-oxabicyclo[2.1.1]hexan-3-one. In a 2-l. flask equipped with mechanical stirrer, thermometer, Claisen head fitted to a receiver with side arm, and oil bath was placed 3-chloro-1-methylcyclobutanecarboxylic acid (98.2 g, 0.66 mol), sodium bicarbonate (111.0 g, 1.32 mol), and dibutyl phthalate (0.4 l.). The mixture was heated under full oil pump vacuum. When the temperature reached 87°, carbon dioxide evolution began and the pressure started to rise. When the pressure returned to 0.5 mm, heating was resumed. At 112° (0.6 mm), the receiver was cooled in Dry Ice–acetone to trap the product as it distilled. The lactone distilled while the inner temperature was raised to 180°. The crude product was transferred to a 500-ml flask and diluted with 0.2 l. of pentane. The solution was filtered through Celite and magnesium sulfate, concentrated, and distilled in an 18-in. spinning band column to yield 17.1 g (23.0%) of 1-methylcyclobutane-1,3-lactone, bp 39° (0.2 mm). This contained by gc 17% of an impurity of shorter retention time and 1% of an impurity with longer retention time. Final purification was effected by recrystallizing three times from ether at −80° and redistilling, bp 33.5° (0.5 mm). This completely eliminated the earlier impurity but the later one was still visible.

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.10, 64.15; H, 7.18, 7.09.

Ir showed 3.31 (two sh, m) and 3.42 (w), CH, 5.53 (s), γ-lactone C=O; nmr τ 5.15 (1 H, s, HCO), 7.62 (4 H's, ring), 8.69 (3 H, s, CH_3).

3-Chloro-3-methylcyclobutanecarboxylic Acid *via* 3-Methylenecyclobutanecarboxylic Acid. In a 3-l. flask fitted with a mechanical stirrer, dropping funnel, and thermometer and cooled in an ice bath was added 1.14 kg of concentrated (12 *N*) hydrochloric acid. To the stirred acid was added 500 g (4.45 mol) of 3-methylenecyclobutanecarboxylic acid at such a rate as to maintain the temperature at 20–25°, and the mixture was stirred vigorously for 5 hr. The organic layer was separated and the aqueous layer was saturated with dry hydrogen chloride at 25° and the above process repeated using an additional 480 g of 3-methylenecyclobutanecarboxylic acid. There was obtained 1070 g (81%) of 3-chloro-3-methylcyclobutanecarboxylic acid (mixture of isomers of about 2:1 ratio on basis of nmr spectrum), bp 121–126° (12 mm), 78–84° (0.5 mm).

Anal. Calcd for $C_6H_9ClO_2$: C, 48.50; H, 6.06; Cl, 23.90. Found: C, 48.25; H, 6.17; Cl, 23.58.

At room temperature, crystals separated from the distillate. These were recovered by filtration and crystallized from petroleum ether. This solid fraction gave no lactone when treated with aqueous sodium bicarbonate. On the basis of nmr spectrum of the solid in carbon tetrachloride, it appeared to be the minor part of the mixture of chlorocarboxylic acids.

***cis*- and *trans*-3-Chloro-3-methylcyclobutanecarboxylic Acid *via* 3-Methylenecyclobutanecarbonitrile.** A 1-l. bomb (Hastelloy B) was charged with 0.57 kg of 12 *N* HCl and 186 g (2 mol) of 3-methylenecyclobutanecarbonitrile and heated at 100° for 8 hr. The cooled mixture was treated with sufficient water to dissolve the ammonium chloride and then extracted with three 200-ml portions of methylene chloride. The methylene chloride extracts were combined, dried over magnesium sulfate, filtered, and the methylene chloride evaporated to leave 240.6 g (81.2%) of oil which partially crystallized on cooling. The nmr spectrum revealed two methyl groups in the ratio of 3:5.

1-Methyl-2-oxabicyclo[2.1.1]hexan-3-one. To an ice cold solution–slurry of potassium bicarbonate (112 g, 1.12 mol) in water (400 ml) was added with stirring and ice bath cooling a mixture of 37.89% *cis*- and 62.2% *trans*-3-chloro-3-methylcyclobutanecarboxylic acid (74.25 g, 0.5 mol). The mixture was stirred at 0° for 0.5 hr after carbon dioxide evolution ceased. The mixture was transferred to a continuous extractor and extracted with ether for 4 hr, during which time the aqueous phase warmed to about 28° and carbon dioxide evolved. The ether phase was washed with a 10% solution of potassium bicarbonate in water and then dried over magnesium sulfate, filtered, and the ether evaporated to leave 16.72 g (30%) of crystalline lactone. Purification was best achieved by recrystallization from hexane followed by sublimation. The lactone purified in this manner had mp 28°, bp 94–96° (21 mm).

Anal. Calcd for $C_6H_8O_2$: C, 64.25; H, 7.14. Found: C, 64.91, 64.82; H, 7.24, 7.35.

***cis*- and *trans*-3-Chloro-1,3-dimethylcyclobutanecarboxylic Acid.** A 1-l. bomb (Hastelloy B) was charged with 570 g of 12 *N* HCl and then 214 g (2 mol) of 1-methyl-3-methylenecyclobutanecarbonitrile. The bomb was heated at 100° for 8 hr, cooled, and sufficient water was added to dissolve the ammonium chloride. The mixture was extracted with three 200-ml portions of methylene chloride, the combined extracts were dried over magnesium sulfate, filtered, and the methylene chloride evaporated. From five runs (1008.7 g of 1-methyl-3-methylenecyclobutanecarbonitrile) there was obtained 1411.6 g (92%) of a 2:3 mixture of isomeric chloro acids. After standing 10 days, a large quantity of crystalline material was present. The oil was drained from the crystals and the crystals recrystallized from hexane to give 235 g of pure *trans*-1,3-dimethyl-3-chlorocyclobutanecarboxylic acid, mp 65–66°. The mother liquors were concentrated at reduced pressure and the residue was combined with the oil phase. The resulting composition of the oil phase was 50:50 cis and trans chloro acids. A sample of the trans chloro acid was analyzed.

Anal. Calcd for $C_7H_{11}ClO_2$: C, 51.70; H, 6.77; Cl, 21.82. Found: C, 52.20, 52.23; H, 6.85, 6.86; Cl, 21.96, 21.89.

1,4-Dimethyl-2-oxabicyclo[2.1.1]hexan-3-one. To an ice cold solution of potassium bicarbonate (115 g, 1.15 mol) in water (550 ml) was added 162.5 g (1 mol) of 3-chloro-1,3-dimethylcyclobutanecarboxylic acid. When carbon dioxide evolution ceased, the solution was warmed to 58° and held at this temperature for 15 min. At 52°, a milky appearance developed and after 15 min at 58° a clear upper lactone layer and clear aqueous phase had developed. The mixture was chilled in ice–water with stirring and the lactone collected on a filter. The aqueous phase was extracted with two 100-ml portions of methylene chloride, the extract dried over magnesium sulfate, and the methylene chloride evaporated. The combined lactone was taken up in hot hexane, dried over magnesium sulfate, filtered, and the filtrate chilled and filtered to give 103.6 g (82.2%) of pure lactone, mp 50.5–51.5°, as colorless, volatile needles.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.60; H, 7.94. Found: C, 66.66, 66.74; H, 8.10, 7.99.

The reaction of 88 g of cis and trans chloro acids with 600 ml of saturated sodium bicarbonate led to 32.5 g (47.8%) of lactone. Since the mixture of chloro acid contained only 58% trans; the anticipated yield based on the trans isomer would be 39.4 g. However, the pure trans isomer gave only an 82% yield of lactone, therefore a more realistic figure would be $0.82 \times 39.4 = 32.4$ g, very close to the amount obtained.

For polymerization the 1,3-dimethyl lactone was crystallized from cyclohexane, sublimed, and resublimed immediately before use.

α-Trifluoromethylacrylonitrile.[5] In a 2-l. three-necked flask equipped with stirrer, additional funnel, Dry Ice condenser, and ice bath was charged a solution of potassium cyanide (111.5 g) in water (430 ml). To this solution was added 187.9 g (1.42 mol) of 1,1,1-trifluoroacetone. To the resulting ice cold solution was added over 5 min a solution of sulfuric acid (88 ml) in water (125 ml). The mixture was stirred for 15 min and the lower organic phase separated. The aqueous phase was extracted with ether and the combined organic phases were dried over magnesium sulfate, filtered, and distilled to give 156.8 g (67.3%) of the cyanohydrin, bp 70–72° (50 mm).

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(5) *Cf.* J. B. Dickey, U. S. Patent 2,541,466 (1951) to Eastman Kodak Co.

To 1,1,1-trifluoroacetone cyanohydrin (156.8 g) was added over 25 min 100 ml of acetyl chloride. The mixture was warmed to gentle reflux and after 1.3 hr an additional 55 g of acetyl chloride was added and refluxing continued for 0.7 hr. Distillation gave 180.8 g (90%) of the cyanohydrin acetate, bp 90–92° (100 mm).

The cyanohydrin acetate was pyrolyzed by passage through a 20 mm × 1 ft tube packed with 0.25-in. Pyrex helices and externally heated at 520°. The tube was swept with a stream of nitrogen (*ca.* 10 ml/min) and the receiver cooled in Dry Ice and protected from atmospheric moisture with a calcium chloride drying tube. The acetate (180.8 g) was pyrolyzed in 4 hr. Distillation of the pyrolysate gave 84.5 g (77.5%) of α-trifluoromethylacrylonitrile, bp 76°.

1-Trifluoromethyl-3-methylenecyclobutanecarbonitrile. In a 500-ml bomb, α-trifluoromethylacrylonitrile (73.6 g), allene (40 g), and benzene (70 ml) with 2 g of hydroquinone were held for 8 hr at 200°. Distillation of the product gave 56.9 g (58%) of the desired cyclobutane, bp 77° (106 mm), $n^{24}{}_D$ 1.3869.

Anal. Calcd for $C_7H_6NF_3$: C, 52.15; H, 3.73; N, 8.70; F, 35.40. Found: C, 52.35, 52.23; H, 3.75, 3.75; N, 9.14, 9.15; F, 35.01.

1-Trifluoromethyl-3-chloro-3-methylcyclobutanecarboxylic Acid. Heating 27.4 g of 1-trifluoromethyl-3-methylenecyclobutanecarbonitrile with 570 g of concentrated hydrochloric acid was carried out at 100° for 8 hr in a 1-l. bomb (Hastelloy B). The product was filtered and the crystalline acid dissolved in ether, dried over magnesium sulfate, filtered, and the ether evaporated to leave 31.21 g (85%) of crystalline product. A sample, recrystallized from hexane and sublimed, was analyzed.

Anal. Calcd for $C_7H_8ClF_3O_2$: C, 38.80; H, 3.69; Cl, 16.39; F, 26.30. Found: C, 38.86; H, 3.47, 3.50; Cl, 16.89, 17.03; F, 26.08.

1-Trifluoromethyl-4-methyl-3-oxabicyclo[2.1.1]hexan-2-one. To a cooled (ice) slurry of 53% sodium hydride–mineral oil dispersion (8.0 g) in 400 ml of ether was added a concentrated ether solution of 3-chloro-3-methyl-1-trifluoromethylcyclobutanecarboxylic acid (37.5 g, 0.173 mol) over 30 min. When the addition was complete, the mixture was heated at reflux for 1 hr and then the ether distilled while Primol D (400 ml) was added. The flask was then equipped with a short distilling head and Dry Ice cooled receiver. The system was evacuated to 1–2 mm and heated at 160–180° for 4 hr. The distillate crystallized and was recrystallized from hexane to give 9.1 g (30%) of lactone as colorless needles, mp 61–62°.

Anal. Calcd for $C_7H_7F_3O_2$: C, 46.65; H, 3.89; F, 31.65. Found: C, 45.73, 45.98; H, 3.61, 3.61; F, 31.66, 31.34.

Triphenylmethylsodium. Triphenylmethylsodium can be prepared conveniently starting with a dispersion of sodium in xylene. A magnetic stirrer appears to be necessary as one attempt to use a mechanical stirrer did not give any triphenylmethylsodium. It may be that the magnetic stirrer crushes the particles of sodium and exposes fresh surfaces that are more reactive than the original dispersion. A slight excess of sodium dispersion was used in most runs, and it was noted that the excess sodium was transformed into thin plates if the stirring was vigorous and prolonged.

A 300-ml flask, fitted with a Teflon-coated stirring bar and a condenser to which a T-tube was attached so that the reaction might be conducted in an atmosphere of nitrogen, was swept with nitrogen and was heated gently to ensure elimination of moisture. When the flask had cooled, 12.5 g (0.045 mol) of recrystallized triphenylchloromethane, 8.6 g of a 30% sodium dispersion in xylene (2.50 g-atom of sodium, 0.112 mol of Na, mole ratio triphenylmethylchloride:Na = 1:2.5) and 140 ml of anhydrous ether was added, the nitrogen flow across the top of the condenser was continued, and the water in the condenser was turned on. The mixture was stirred vigorously to keep the sodium suspended. The ether solution became yellow in color and after about 1.0–1.5 hr, a slight exothermic reaction set in and the ether refluxed gently. After an additional period of 10–15 min, a deep red color developed and the exothermic reaction ceased within about 11–20 min after development of the red color. The reaction appeared complete after stirring for 1 hr as judged by titration of a test sample. However, to ensure complete reaction, the reaction mixture was stirred 2–16 hr after development of the red color. The reaction mixture was allowed to stand for 1 hr (or more), and the solution was filtered under pressure into a glass stoppered bottle flushed with nitrogen and fitted with a three-way stopper so that samples could be removed under an atmosphere of nitrogen. Two milliliters of the solution was run into water and the solution was titrated with 0.100 *N* HCl, using methyl red as the inidicator. The solution was 0.30 *N* with respect to triphenylmethylsodium. A second run titrated 0.315 *N* (the volume was slightly less than 150 ml) and was combined with the first run. The combined two runs titrated 0.307 *N*, and after standing for 39 days, the solution was 0.305 *N*.

Polymerizations. Xylene was dried by distillation and stored under nitrogen over sodium where all reaction vessels were flamed under nitrogen immediately before use.

With Sodium. Into a long 15-mm glass tube fitted with a ground glass joint at the top were charged xylene and the molten lactone. The tube was flushed for 4 min with nitrogen flowing at the rate of 200 ml/min. Clean sodium, ~0.05 g, was added, and the reaction vessel was closed with a glass stopper. The reaction vessel was placed in an oil bath at 70–72° and allowed to remain for 8 days. The resulting solid was broken up with a metal rod, ether was added, the solid was collected and washed with ether. To neutralize the initiator, the solid was refluxed with methanol containing a few drops of acetic acid. During this treatment, the color of the polyester changed from blue to white. The polyester was collected, washed first with methanol, then ether, and dried at 50–60° (15–20 mm). The yield of polyester was 2.55 g. It had an inherent viscosity of 2.28 (phenol:1,1,2-trichloroethane (60:40) 0.5%, 30°).

In another experiment, into a dry 6-in. glass test tube was placed, under an atmosphere of nitrogen, ~0.05 g of freshly cut sodium. This was ground against the bottom of the tube with a glass rod to expose a large area of fresh metal. 1-Methyl-2-oxabicyclo[2.1.1]hexan-3-one was added and the tube was tightly sealed and placed in an oil bath at 70°. Polymerization proceeded slowly with solid polymer growing outward from the surface of the sodium. After 48 hr at 70° most of the molten monomer was converted to white polymer. This polymer had an inherent viscosity (determined at 0.5% concentration in chloroform) of 5.0. This polymer was soluble in chlorobenzene and the resulting chlorobenzene solution could be cast into a film which, after drying, was drawn at 125° to give a crystalline, oriented film with a wide-angle X-ray orientation of 15°. This polymer became quite workable after standing several minutes at 225° and long fibers were pulled from the melt. These fibers were readily drawn at 50° with characteristic necking down of the fiber. The oriented fibers, after boiling off taut, had the following properties: tenacity, 2.5 g/denier; elongation at break, 55%; initial modulus, 23 g/denier.

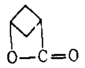
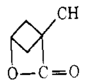
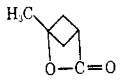
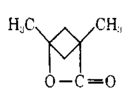
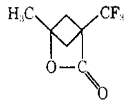
With Potassium. If potassium was the initiator, within a few minutes blue polymer appeared on the piece of potassium, and the initiator and polymer sank to the bottom of the reaction vessel. The polymerization continued slowly until a solid, granular mass resulted. The polymerizations were allowed to proceed for 16–120 hr. Anhydrous ether was added, the resulting granular product was collected, washed with ether to remove xylene and monomeric lactone, refluxed with methanol containing a few drops of acetic acid, and dried at 50–55° (15–20 mm).

With NaK. Using a small drop of liquid NaK, added with a syringe, made it possible to run the polymerizations at lower temperatures, leading to somewhat higher inherent viscosities. The blue color of the polymerization mass suggested that an ion radical might be present, but no radical could be detected by epr measurements.

With Triethylaluminum. The lactone (10 g), 1-methyl-2-oxabicyclo[2.1.1]hexan-3-one, was polymerized with approximately 7 mg of an 0.82 *M* solution of triethylaluminum in hexane as catalyst at 60°. After 16 hr of polymerization, there was obtained a 99% yield of a solid polymer having an inherent viscosity (determined at 0.5% concentration in trifluoroacetic acid) of 0.60. This polymer did not melt to a free flowing liquid but became rubbery. At 275° the polymer decomposed quite rapidly.

With BF_3. A dry 6-in. test tube was charged with 0.9 g of 1-methyl-4-trifluoromethyl-2-oxabicyclo[2.1.1]hexan-3-one and the tube

Table I
Polymerization of 2-Oxabicyclo[2.1.1]hexan-3-ones

Lactone	Amt, g	Xylene, ml	Initiator	Temp, °C	Time, hr	Yield, g	Yield, %	η_{inh}[a]	Mp, °C (DTA, 2 cycles)
	1.0		Tetraisopropyl titanate, 0.01 ml	150	1.8	0.98	98	0.26	236
	1.0		$NaOCH_3$, 0.01 g	150	1.8	0.80	80	0.41	242
	31.0		Tetraisopropyl titanate	100		0.64	64	0.23	154
	1.0		$NaOCH_3$, 0.01 g	100	2 (no poly)	0.53	53		
				150	2 (no poly)				
				150	16 (complete)				
			$(C_2H_5)_3Al$, 0.01 ml	100	2 (slow)				
				150	2 (complete)	0.26	26	0.23	245
	2.0	1.7	NaK	45	44	1.7	85	3.33	
	2.2	2.3	NaK	45	20	2.1	91	3.20	
	2.8		K	65–70	48	2.1	75	1.90	
	4.1	3.9	K	65–70	90	3.2	78	2.46	
	2.0	3.0	$(C_6H_5)_3CNa$	50	20	0.6	29	2.55	
	5.0	50.0	KOC_4H_9-*tert*	35	20	3.6	72	1.83	
	2.0	10.0	$(C_6H_5)_3COK$	60	3	1.9	95	1.22	
	1.6	2.4	$(C_2H_5)_3Al$	42	18	1.0	60	0.81	
	1.6	2.4	$(i\text{-}C_4H_9)_2AlCl$	55	20	0.4	22	0.30	
	5.0	50	Na, $C_{10}H_8$	35	8	1.5	30	0.85	
	2.0	2.0	NaK	42	20	2.0	100	3.43	
	2.0	2.0	NaK	42	118	1.8	90	3.38	
	3.0	4.5	NaK	45	70	2.7	90	3.81	
	2.0	3.2	Na	75	188	1.7	85	2.06	
	1.6	2.4	$(C_6H_5)_3CNa$	55	20	1.5	94	0.89	
	1.6	2.4	$(C_2H_5)_3Al$	55	70	0.6	41	0.88	
	0.9		$BF_3 \cdot C_2H_5OC_2H_5$	68	1.5	0.5	55	0.52	

[a] Trifluoracetic acid, 0.1%, 30°.

was stoppered. The tube was then heated at 68° and when the lacton was molten approximately 0.001 ml of boron trifluoride etherate was added. Polymerization took place rapidly with formation of a solid white polymer. After 1.5 hr of polymerization at 68°, the polymer was dissolved in ten parts of trifluoroacetic acid. This solution was poured with stirring into 100 parts of methanol, whereupon the polymer precipitated. The polymer was separated by filtration and then air dried. There was obtained 0.5 g of white polymer which had an inherent viscosity of 0.52 (determined at 0.1% concentration in trifluoroacetic acid at 25°). Samples of this polymer could be pressed at 100° into clear self-supporting films.

Copolymerization with Pivalolactone. Pivalolactone (2 g), 2 g of 1,4-dimethyl-2-oxabicyclo[2.1.1]hexan-3-one, and 0.02 g of sodium methoxide were heated together in a reaction vessel fitted with a condenser and mechanical stirrer. Polymerization occurred at 100° giving a solid product which melted at a bath temperature of 200°. The reaction mixture was heated at 200° for 3 hr, then cooled, triturated with hexane, and filtered to give 3.5 g of copolymer of pivalolactone and 1,4-dimethyl-2-oxabicyclo[2.1.1]hexan-3-one melting at 190–192° by DTA. This copolymer could be melt pressed at 170° into a clear film. The inherent viscosity of the polymer was 0.19 (measured in trifluoroacetic acid at 0.5% concentration).

The results of other polymerization experiments are given in Table I. Carbon–hydrogen analyses and infrared spectra confirmed the assigned structures.