Synthesis and Polymerization of Bridgehead-Substituted Bicyclobutanes

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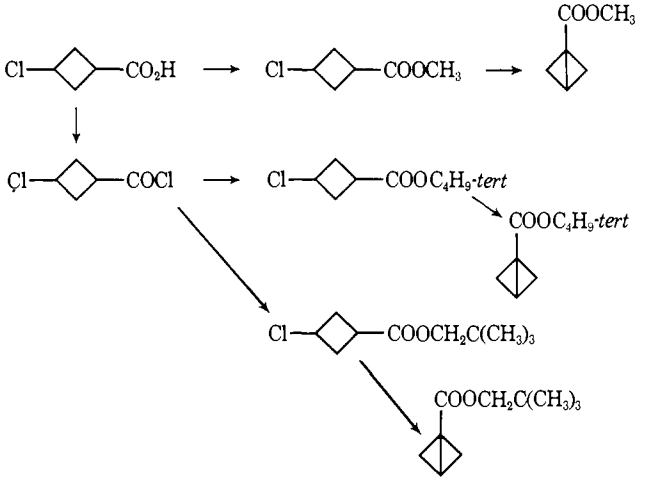
Abstract: Bicyclobutanes carrying ester, acid, amide, and acyl functions at the bridgehead were synthesized. When the other bridgehead was unsubstituted or, in one case, carried an ester group, free-radical polymerization was successful. However, a 3-methyl or 3-phenyl group suppressed polymerization. It was advisable to use a mild chain-transfer agent to avoid gel. In contrast, bicyclobutanes carrying only hydrogen, phenyl, or methyl at the bridgehead were not successfully polymerized. They did not copolymerize with vinyl monomers, giving only gelled and highly branched products. We concluded that if the bridgehead substituent can stabilize an adjacent free radical, propagation occurs; otherwise, the hot radical abstracts tertiary hydrogen from adjacent chains. The hydrocarbons did copolymerize with SO_2 to give polysulfones. A few reactions and calculations of isomerization equilibria for these compounds are reported.

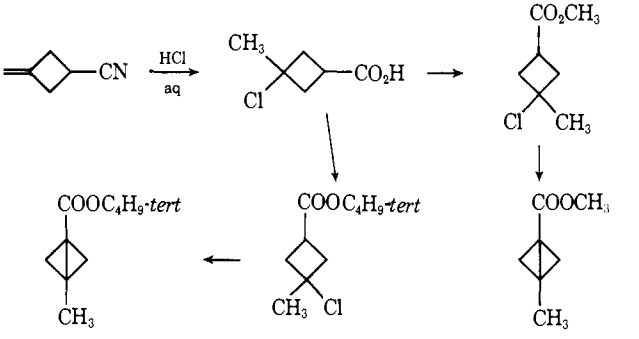
The preceding article[2] showed that 1-bicyclobutanecarbonitriles, polymerizing through the strained 1,3 bond, constituted a new class of reactive monomers. To explore the effects of bridgehead substituents on polymerization, we have studied the synthesis and polymerization of a variety of substituted bicyclobutanes.

Esters. 3-Chlorocyclobutanecarbonitrile[2] readily underwent hydrolysis by hydrochloric acid to form 3-chlorocyclobutanecarboxylic acid. Direct esterification of the chloro acid and dehydrochlorination formed methyl 1-bicyclobutanecarboxylate.[3] As in the case of the chloronitriles, the 3-chloro group was amply reactive in the cyclization step. Other chloro esters

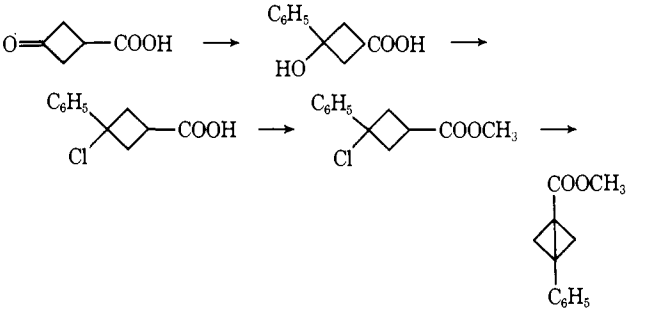


were formed when the acid chloride was treated with *tert*-butyl alcohol or neopentyl alcohol. Dehydrochlorination gave the corresponding bicyclobutane esters.

3-Methylenecyclobutanecarbonitrile was converted by refluxing concentrated hydrochloric acid to 3-chloro-3-methylcyclobutanecarboxylic acid. Esterification with methanol or isobutylene gave the corresponding esters. Dehydrochlorination gave the corresponding bicyclobutanes.[4]



Reaction of 3-oxocyclobutanecarboxylic acid[5] with excess phenylmagnesium bromide gave 3-phenyl-3-hydroxycyclobutanecarboxylic acid, which on successive treatment with concentrated hydrochloric acid, diazomethane, and sodium hydride gave methyl 3-phenyl-1-bicyclobutanecarboxylate.



1-Chloro-1,3-cyclobutanedicarbonitrile[2] was converted with methanol and anhydrous hydrogen chloride to dimethyl 1-chlorocyclobutane-1,3-dicarboxylate

(1) Chestnut Run Film Department Laboratory, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

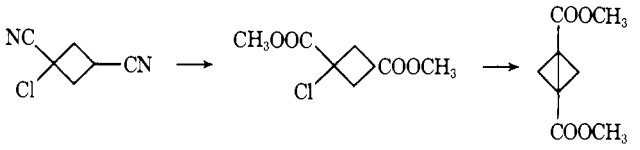
(2) See preceding article: H. K. Hall, Jr., E. Blanchard, Jr., S. Cherkofsky, J. Sieja, and W. Sheppard, *J. Amer. Chem. Soc.*, **93**, 110 (1971).

(3) (a) K. B. Wiberg, *Rec. Chem. Progr.*, **26**, 143 (1965); (b) K. B. Wiberg, *Tetrahedron*, **21**, 2749 (1965).

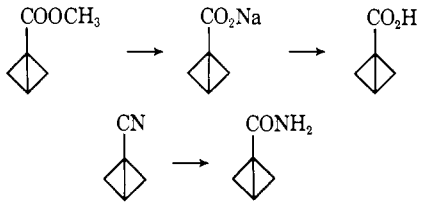
(4) We are indebted to Dr. A. Cairncross for this synthesis. The methyl 3-methylbicyclobutanecarboxylate was prepared independently by Wiberg and coworkers.[3]

(5) J. D. Roberts and F. F. Caserio, *J. Amer. Chem. Soc.*, **79**, 5837 (1957).

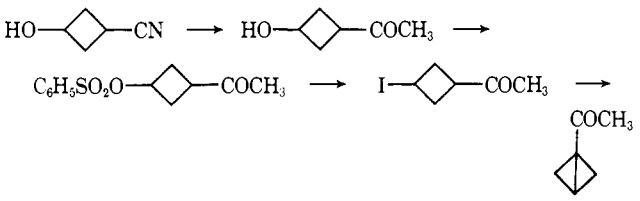
Treatment with base gave dimethyl 1,3-bicyclobutanecarboxylate.[6]



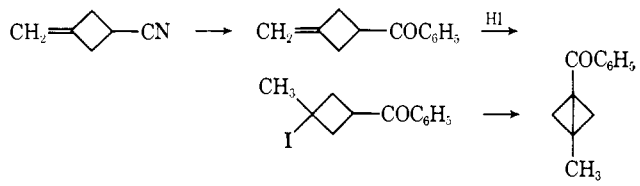
Acids and Amides. Saponification of methyl 1-bicyclobutanecarboxylate led to the corresponding sodium salt and thence to the crystalline free acid. Base-catalyzed peroxide converted 1-bicyclobutanecarbonitrile into the corresponding carboxamide. 3-Methylbicyclobutane-1-carboxamide had been prepared earlier by an analogous reaction.[7]



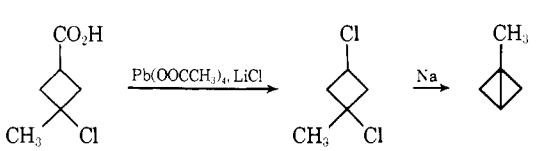
Ketones. Reaction of 3-hydroxycyclobutanecarbonitrile with excess methylmagnesium iodide gave 3-acetylcyclobutanol. This was converted to the sulfonate, the iodide, and to 1-acetylbicyclobutane.

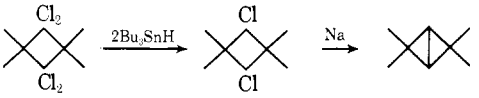


Reaction of 3-methylenecyclobutanecarbonitrile with phenylmagnesium bromide, followed by hydrogen iodide and NaH, gave 3-methyl-1-benzoylbicyclobutane.



Hydrocarbons. Bicyclobutane[3] and its 1-phenyl and 1-vinyl derivatives were available *via* the cycloaddition of ketene to vinyl ethers investigated by Sieja.[8] Decarboxylative chlorination[9] of 3-methyl-3-chlorocyclobutanecarboxylic acid gave the 1,3-dichloride, which with sodium furnished 1-methylbicyclobutane. 2,2,4,4,-Tetramethylbicyclobutane was prepared from the readily accessible 2,2,4,4-tetramethyl-1,1,3,3-tetrachlorocyclobutane[10] as follows. Recently,



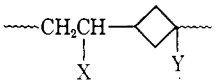


five 2,2,4,4-tetramethylbicyclobutanes have been prepared but not isolated.[8,11-15]

Homopolymerizations. The bicyclobutanes were subjected to radical, cationic, anionic, and coordination polymerization conditions. Only the radical polymerizations gave good yields of high polymers. These experiments are summarized in Table I. The bicyclobutanes with electronegative substituents (COOR, $CONH_2$, $COCH_3$) at the bridgehead polymerized well under free-radical conditions. Methyl 1-bicyclobutanecarboxylate[3] and methyl 2,2,4,4-tetramethylbicyclobutanecarboxylate[13] polymerize when left at room temperature. It was necessary in some cases to add a weak chain-transfer agent like isobutyraldehyde to avoid some gel formation. 1-Vinylbicyclobutane also polymerized but, unexpectedly, the 1-phenyl derivative did not. 3-Methyl or 3-phenyl substituents on methyl 1-bicyclobutanecarboxylate suppressed polymerization but a 3-methoxycarbonyl substituent could be tolerated.

Bicyclobutanes with only methyl or hydrogen at the bridgehead did not polymerize well. 1-Methylbicyclobutane gave oligomers with BF_3. Irradiation with uv light converted bicyclobutane and 2,2,4,4-tetramethylbicyclobutane to cross-linked polyhydrocarbons in low conversions. The former gave oligomers with π-allyl nickel bromide, and dimers with other coordination or cationic initiators. The dimer mixture contained olefinic and cyclopropane hydrogens by nmr and contained at least four dimers by gc and mass spectral analysis.

Copolymerizations with Vinyl Monomers. Bicyclobutanes with groups which are particularly good at stabilizing radicals copolymerized smoothly with vinyl monomers to yield copolymers containing 1,3-cyclobutane rings in the chain. Similar copolymers with Y = CN had been prepared previously.[2] The 1-phenyl

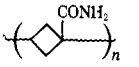
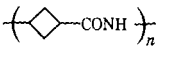


derivative did not copolymerize with styrene under radical or anionic conditions. Bicyclobutane copolymerized with acrylonitrile or methyl methacrylate to give cross-linked copolymers. Bicyclobutane and its 1-methyl derivative copolymerized readily with sulfur dioxide to give 1:1 polysulfones. Table II summarizes the results.

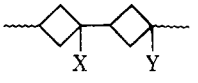
Copolymerizations of Two Bicyclobutanes. Free-radical copolymerizations of bicyclobutanes carrying electronegative substituents with one another were accomplished readily to yield copolymers containing 1,3-cyclobutane links only. The cyano compounds

(6) This compound was first prepared another way by Dr. C. E. Coffey of the du Pont Explosives Department, who we thank for instructions and samples.
(7) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487 (1966).
(8) See accompanying article: J. B. Sieja, *ibid.*, **93**, 130 (1971).
(9) J. Kochi, *ibid.*, 87, 2500 (1965).
(10) H. G. Gilch, *J. Org. Chem.*, **30**, 4392 (1965).
(11) M. R. Rifi, *J. Amer. Chem. Soc.*, **89**, 4442 (1967).
(12) D. P. G. Hamon, *ibid.*, **90**, 4513 (1968).
(13) C. Burridge and D. P. G. Hamon, *Chem. Commun.*, 206 (1968).
(14) M. F. Neumann, *Angew. Chem., Int. Ed. Engl.*, **6**, 79 (1967).
(15) E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967).

Table I. Homopolymerizations of Bicyclobutanes

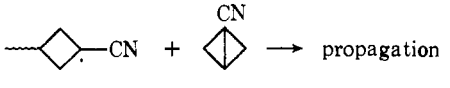
Monomer	Amt, g	Solvent	Amt, ml	Initiators	Amt, g	Temp, °C	Time, hr	Yield, g	η_{inh}[a]	Comments
Methyl bicyclobutane-1-carboxylate		Polymerized spontaneously								Sparkling clear tough plug
Methyl bicyclobutane-1-carboxylate	1.0	H_2O	10	Standard emulsion recipe		50	3.5	1.0	4.86	
Methyl bicyclobutane-1-carboxylate	0.6	H_2O Soap soln	3.5 0.7	Azobisisobutyronitrile		50	16	0.6	5.60	
Methyl bicyclobutane-1-carboxylate	3.2	DMSO	10	Azobisisobutyronitrile	0.1	50	16	High		Rigid gel
Methyl bicyclobutane-1-carboxylate	3.2	DMSO	10	Azobisisobutyronitrile Isobutyraldehyde	0.1 0.25 (ml)	50	16	2.5	1.60	
Methyl bicyclobutane-1-carboxylate	1.0	Hexamethylphosphoramide	5	NaH soln	0.2	Room temp	16	High	0.63	Brittle hazy film from $CHCl_3$
tert-Butyl bicyclobutane-1-carboxylate	4.0	2-Butanone	10	Azobisisobutyronitrile	70 (mg)	60–65	24	High	0.23	DTA, endotherm 130–140°, dec 220–240°
Methyl 3-methylbicyclobutane-1-carboxylate	1.3	Tetramethylene sulfoxide	14	α,α'-Azobis(α,γ-dimethylvaleronitrile)	0.05	75 6000 atm	4	0.95	0.70	
tert-Butyl 3-methylbicyclobutane-1-carboxylate	1.3	Tetramethylene sulfoxide	14	α,α'-Azobis(α,γ-dimethylvaleronitrile)	0.05	75 6000 atm	4	0.90	0.74	
Dimethyl 1,3-bicyclobutanedicarboxylate	4.0	H_2O	50	Dipotassium phosphate 3% aq polymethacrylic acid 0.18 *M* Vazo in methanol	0.22 0.43 0.3 (ml)	Up to 160	3	2.29	2.55	
Dimethyl 1,3-bicyclobutanedicarboxylate	3.0			Di-*tert*-butyl peroxide	37 (mg)	65	1	High		Tough sparkling colorless solid plug
Bicyclobutane-1-carboxylic acid	0.72	DMSO	4	Azobisisobutyronitrile Isobutyraldehyde	0.05 0.1 (ml)	50	16	0.45	4.29	Inherent viscosity 0.1% in 0.5% NaOH at 25°
Bicyclobutane-1-carboxamide	1.08	DMSO	6	Azobisisobutyronitrile	0.05	60	16	1.05	6.63	Inherent viscosity 0.1% in formic acid at 25° Ir only primary amide 
Bicyclobutane-1-carboxamide	1.0	DMSO	2	Potassium *tert*-butoxide	0.05	60	2	0.1		Ir secondary amide 
1-Acetylbicyclobutane	7.8	H_2O	150	Standard emulsion recipe		50	1	3.5	1.12	
1-Acetylbicyclobutane	5.0	DMSO	25	Benzoyl peroxide	0.01	Room temp	24	3.0	2.34	

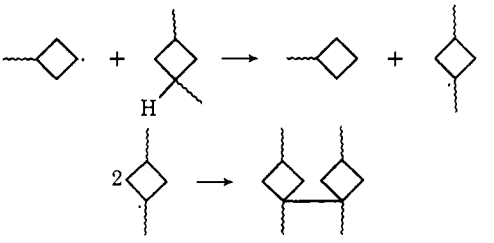
[a] 0.1% in chloroform unless otherwise noted.



prepared earlier[2] were particularly facile. Copolymerizations with bicyclobutane led to highly cross-linked polymers.

We think that successful free-radical polymerization depends on the competition between propagation and chain transfer to polymer. If the substituent is cyano, the growing radical is relatively stable and discriminating, and propagation to a new stable radical is favored. Also, the reactivity of the tertiary hydrogens in the polymer chain is lowered by the adjacent cyano group. As the substituent is less able to stabilize the radical (in the extreme, bicyclobutane itself), the unstabilized radical is not discriminating, has little tendency to propagate to a new "hot" radical, and prefers to abstract the reactive tertiary hydrogens of the polymer. Dimerization of such radicals leads to cross-linking and gel formation.





Isomerizations. During attempts to polymerize 1-phenylbicyclobutane we observed ready isomerization to 1-phenylcyclobutene. This raised the question of the exact position of equilibrium in such reactions.

Heats of formation for bicyclobutane and cyclobutene[16–18] show that the latter is much more stable.

(16) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968).
(17) A. Danti, *J. Chem. Phys.*, 27, 1227 (1957).
(18) *Nat. Bur. Stand. (U. S.) Circ.*, No. **500**, 477, 527, 571 (1952).

Table II. Copolymerizations of Bicyclobutenes

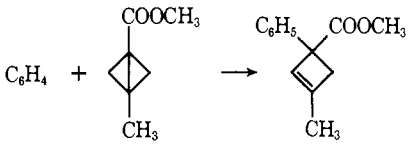
Monomer	Amt, g	Comonomer	Amt, g	Solvent	Amt, ml	Initiator	Amt, mg	Temp, °C	Time, hr	Yield, g	η_{inh}	Comments
Methyl bicyclobutane-1-carboxylate	4.0	1-Bicyclobutanecarbonitrile	4.0	Tetramethylene sulfoxide	40	Azobisisobutyronitrile	50	70	16	6.7	0.89	*Anal.* corresponds to 42% nitrile and 58% ester in polymer
Methyl bicyclobutane-1-carboxylate	4.0	Dimethyl bicyclobutane-1,3-dicarboxylate	4.0	Tetramethylene sulfoxide	40	Azobisisobutyronitrile	50	70	16	4.2	0.99	*Anal.* corresponds to 35% diester and 65% ester in polymer
Dimethyl bicyclobutane-1,3-dicarboxylate	4.0	1-Bicyclobutanecarbonitrile	4.0	Tetramethylene sulfoxide	40	Azobisisobutyronitrile	50	70	16	5.8	0.74	*Anal.* corresponds to 75% nitrile and 25% diester in polymer
1-Bicyclobutanecarboxamide	2.0	Acrylonitrile	1.0	DMSO	4	Azobisisobutyronitrile	50	50	16	0.72		*Anal.* corresponds to 25% amide and 75% acrylonitrile in polymer
1-Bicyclobutanecarboxamide	0.81	Acrylamide	0.3	DMSO	4	Azobisisobutyronitrile	50	50	16	1.0		*Anal.* corresponds to 84% 1-bicyclobutanecarboxamide and 16% acrylamide in polymer
1-Acetylbicyclobutane	10	Methyl vinyl ketone	10	H_2O	200	Standard slurry recipe		50	1	10	0.62	
1-Acetylbicyclobutane	1.5	Acrylonitrile	8.5	H_2O	200	Standard slurry recipe		50	2	6.6	1.99	
Bicyclobutane	2.1	Acrylonitrile	2	Hexane	10	Et_3B, O_2		−20	16	High		Cross-linked; *anal.* correspond to 25–27% bicyclobutane incorporated
Bicyclobutane	1	Acrylonitrile	1	γ-Butyrolactone	3	Benzoin methyl ether, *hν*		28	16	1.6	1.62	Lightly cross-linked; *anal.* correspond to 33–44% bicyclobutane incorporated
Bicyclobutane	1	Methyl methacrylate	3.0	None		Benzoin methyl ether, *hν*		28	16	3.9		Colorless plug; some cross-linking; *anal.* corresponds to 14% bicyclobutane incorporated
Bicyclobutane	0.9	SO_2	3 (ml)	SO_2 in 25 ml of H_2O Bicyclobutane in 10 ml of benzene added dropwise	10	None		−10	1	0.8	0.68	Inherent viscosity 0.1% in H_2SO_4, 25°. *Anal.* Calcd: S, 27.15. Found: S, 25.30
2,2,4,4-Tetramethylbicyclobutane	1.3	SO_2	5 (ml)	None		None		−78 Room temp	1 16	0.22		*Anal.* Calcd: S, 18.4. Found: S, 16.9
1-Vinylbicyclobutane	2	Acrylonitrile	0.667	H_2O	5.2	8 mg potassium persulfate 80 mg of Duponol ME 19 mg of lauryl mercaptan		37	22	0.57		Cross-linked; *anal.* corresponds to 60% vinylbicyclobutane and 40% acrylonitrile in polymer

From the ir fundamentals, we calculated the thermodynamic properties of bicyclobutane and the following equilibrium constants (Table III).

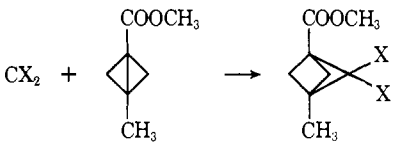
Table III

Temp, °K	K	K
298	2.1×10^{-9}	2.2×10^{-11}
400	2.0×10^{-7}	1.1×10^{-8}
500	2.7×10^{-6}	4.0×10^{-7}
600	1.4×10^{-5}	4.4×10^{-6}
700	4.9×10^{-5}	2.5×10^{-5}
800	1.2×10^{-4}	9.1×10^{-5}

Miscellaneous Chemical Reactions. Benzyne reacted as an electrophile[19,20] to form the cyclobutene ester,



and dihalocarbenes generated by mild conditions[21] added across the central bond of the same ester to give bicyclo[1.1.1]pentanes in low yields.



X = Cl, Br

Experimental Section

General procedures are given in ref 2.

3-Chlorocyclobutanecarboxylic Acid. A mixture of 450 g (3.89 mol) of 3-chlorocyclobutanecarbonitrile[2] and 3 l. of concentrated HCl was stirred at reflux for 20 hr. The mixture was cooled and 450 ml of H_2O was added. The organic layer was extracted with one 2-l. portion of CH_2Cl_2 and then two 0.3-l. portions of CH_2Cl_2. The combined CH_2Cl_2 layers were dried, filtered, and concentrated on the steam bath. Distillation of the crude product gave 440.3 g (84%) of 3-chlorocyclobutanecarboxylic acid, bp 83–86° (0.5 mm) (lit.[22] bp 107–115° (4 mm)), which partly crystallized on keeping: ir 3.37 (s, broad, CH), 3.5–4 (w, OH), 5.85 (s, CO_2H); nmr τ −2.1 (s, 1, carboxyl), 5.38 (s, 1, adjacent to Cl), 7.22 (m, 5, ring). *Anal.* Calcd for $C_5H_7O_2Cl$: C, 44.62; H, 5.24; Cl, 26.34. Found: C, 45.04, 45.25; H, 5.32, 5.48; Cl, 26.35.

3-Chlorocyclobutanecarbonyl Chloride. A mixture of 52 g (0.37 mol) of 3-chlorocyclobutanecarboxylic acid and 280 g of thionyl chloride was heated under reflux for 4 hr. The excess thionyl chloride was distilled off at atmospheric pressure and the 3-chlorocyclobutanecarbonyl chloride was distilled through a short Claisen column under water aspirator pressure to give 52.5 g (80%) of a colorless liquid: bp 70° (18 mm); ir 3.31 (m), 3.36 (m), 3.48 (w, CH), 5.59 (s, acid chloride). *Anal.* Calcd for $C_5H_6Cl_2O$: C, 39.20; H, 3.94; Cl, 46.40. Found: C, 39.28; H, 4.23; Cl, 46.40.

3-Chloro-3-methylcyclobutanecarboxylic Acid from 3-Methylenecyclobutanecarbonitrile. A 1-l. Hastelloy B bomb was charged with 1.25 lb 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, and filtered, and the methylene chloride was 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.

3-Chloro-3-methylcyclobutanecarboxylic Acid from 3-Methylenecyclobutanecarboxylic Acid. In a 2-l. creased flask fitted with mechanical stirrer, dropping funnel, and ice bath was charged 1.25 lb of 12 *N* HCl. To the cold acid was added over 15 min 3-methylenecyclobutanecarboxylic acid (224 g, 2 mol) and the mixture was vigorously stirred for 2 hr. The cold solution was extracted with three 100-ml portions of methylene chloride, the combined extracts were dried over magnesium sulfate, and filtered, and the methylene chloride was evaporated. The combined product from two such runs equaled 480.6 g (81%) and based on the nmr spectrum consisted of a mixture of isomers in the ratio of *ca.* 5:3: ir 3.35 (s), 3.47 (m, CH), 3.5–4 (m, broad, carboxyl), 5.85, 5.91 (s, carboxyl C=O), 7.23 (s) methyl; nmr τ −2 (s, 1, carboxyl), 7.30 (m, 5, ring), 8.27, 8.32 (two s, 3, methyl). *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.

3-Hydroxy-3-phenylcyclobutanecarboxylic Acid. To a solution of 147.8 g (1.3 mol) of 3-oxocyclobutanecarboxylic acid[5] in 1.5 l. of tetrahydrofuran was added, over 6 hr at 20–30°, somewhat more than 2.6 mol of phenylmagnesium bromide in ether. At the end of the addition, the solution should give a positive test for organometallics (Michler's ketone and iodine). The solution was cooled, and 600 ml of 50% hydrochloric acid was added. The organic layer was dried and the solvent removed. The semisolid residue was dissolved in aqueous bicarbonate, which was then extracted twice with ether. Acidification of the aqueous solution with concentrated hydrochloric acid gave 145 g of product, mp 142–143°. The original aqueous phase was combined with the filtrate obtained from the last step. The combined solution was extracted with ether for 24 hr. Removal of the ether gave a gummy solid which was converted directly to 3-chloro-3-phenylcyclobutane carboxylic acid. The total yield of hydroxy acid was 75%.

The hydroxy acid is probably a mixture of cis and trans isomers, but no attempt was made to separate them. The nmr ($(CD_3)_2CO$) shows δ 7.5, multiplet (7 H's, 5 aromatic 1-OH, 1-CO_2H), 2.7, broad singlet (6 H's, cyclobutyl; high value due to solvent impurities). Upon addition of D_2O the nmr shows δ 7.5 multiplet (5 H's), 2.7 broad singlet (5 H's), and 4.3 singlet (2.4 H's).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 69.41; H, 6.34.

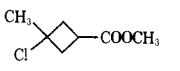
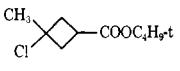
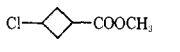
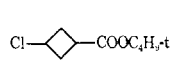
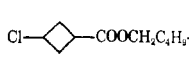
3-Chloro-3-phenylcyclobutanecarboxylic Acid. A 500 ml separatory funnel was charged with 300 ml of benzene, 21.4 g (0.11 mol) of 3-hydroxy-3-phenylcyclobutanecarboxylic acid, and 100 ml of concentrated hydrochloric acid. The mixture was shaken vigorously until all the solid had dissolved (about 3 min). The layers were separated, and the aqueous layer was washed with two 50-ml portions of benzene. The combined organic phase was washed twice with water and twice with brine, the last wash being neutral. The benzene layer was dried over magnesium sulfate, and solvent was removed to give 23.8 g (0.11 mol, 100%) of a dry, white solid. Although no attempt was made to separate isomers, two different fractions were obtained on recrystallization from benzene: mp 110–118°, nmr δ 12.0 singlet (1 H), 7.35 singlet (5 H's), 3.4–4.0 multiplet (1 H), 2.9–3.2 broad doublet (4 H's); mp 82–85°, nmr δ 12.2 singlet (1 H), 7.35 multiplet (5 H's), 2.7–4.0 broad band (5 H's).

Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.70; H, 5.26; Cl, 16.83. Found: C, 62.29; H, 5.21; Cl, 16.65.

Representative Chloro Ester Synthesis. Methyl 3-Chlorocyclobutanecarboxylate. A mixture of 151.9 g (1.13 mol) of 3-chlorocyclobutanecarboxylic acid, 30 ml of methanol, 175 ml of 2,2-dimethoxypropane, and 1.10 g of methanesulfonic acid was stirred under nitrogen at 65°, for 17 hr. Volatile materials were distilled at 65° at approximately 200 mm. The liquid was cooled and mixed with 150 ml of methylene chloride and 150 ml of aqueous potassium chloride. After shaking, the methylene chloride layer was separated and washed with 150 ml of saturated aqueous sodium bicarbonate solution. The methylene chloride layer was separated, dried with magnesium sulfate, and distilled in a spinning-band column. The product, bp 95.2–101.9° (43 mm) (lit.[22] bp 125–128° (100 mm), weighed 144.8 g (86.3%). Gc analysis showed it to consist of 87.6% of one isomer and 12.3% of the other, combined purity 99.9%. Characterization of this and other chloro ester intermediates is given in Table IV.

(19) H. H. Wasserman and J. Solodar, *J. Amer. Chem. Soc.*, **87**, 4003 (1965).
(20) M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968).
(21) F. Nerdel and J. Buddrus, *Tetrahedron Lett.*, **40**, 3585 (1965).
(22) W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962).

Table IV. Preparation of Chloro Ester Intermediates

cis- + *trans*-chloro ester	Reaction	Yield, %	Bp, °C	Analysis, %	Ir	Nmr
	Acid + dimethoxypropane[a]	95	39 (0.8)	$C_7H_{11}O_2Cl$: C, 51.72; H, 6.82; Cl, 21.78 Found: C, 51.75; H, 6.61; Cl, 21.31	5.70 (s) (ester C=O), 3.41 (s), 3.52 (m), (CH) 7.25 (m) (CH_3)	τ 6.31 (3, s, OCH_3), 8.25, 8.32 (3, s, CH_3), 7.32 (5, m, ring)
	Acid + isobutylene[b]	76	47 (0.6)	$C_{10}H_{17}ClO_2$: C, 58.67; H, 8.37; Cl, 17.32 Found: C, 59.70, 59.17, 59.85; H, 8.49, 8.74, 8.92; Cl, 16.64	3.35 (s) (CH) 5.78 (s) (ester C=O) 7.18 (m) 7.31 (m) (methyl) 8–9 (s) (C—O)	τ 7.35 (m, 5, ring), 8.28, 8.32 (s, 3, methyl), 8.56 (s, 9, *tert*-butyl
	Acid + dimethoxypropane	95		$C_6H_9O_2Cl$: C, 48.49; H, 6.11; Cl, 23.86 Found: C, 48.71; H, 6.25; Cl, 23.11	3.36 (s), 3.42 (s), 3.53 (w) (CH), 5.76 (s) (ester, carbonyl), 8.9 (s) (C—O)	τ 5.45 (q, 1, adjacent to Cl), 6.32 (s, 3, methoxyl), 7.28 (m, 5, ring)
	Acid chloride + alcohol + *N*,*N*-dimethylaniline	83	34.5–35 (0.15)	$C_9H_{15}O_2Cl$: C, 56.71; H, 7.94 Found: C, 56.78, 56.62; H, 7.50, 7.49	3.32 (m) (CH), 5.78 (s), (ester C=O) 7.17 (s), 7.32 (s) (methyl)	τ 5.59 (m, 1, adjacent to Cl) 7.36 (m, 5, ring), 8.56 (s, 9, *tert*-butyl)
	Acid chloride + alcohol + *N*,*N*-dimethylaniline	71	56.0–60.5 (0.5)	$C_{10}H_{17}O_2Cl$: C, 58.70; H, 8.38 Found: C, 58.67, 58.49; H, 8.38, 8.38	3.36 (m), 3.47 (w) (CH), 5.76 (s) (ester C=O), 7.25 (m), 7.32 (m) (methyl)	τ 5.53 (p, 1, adjacent to Cl), 6.20 (two s, 2, OCH_2), 6.76 (m. 1, α), 7.32 (m, 4, ring), 9.06 (s, 9, *tert*-butyl)

[a] N. B. Lorette and J. H. Brown, Jr., *J. Org. Chem.*, **24**, 261 (1959). [b] A. L. McCloskey, G. S. Fonken, R. W. Kluiber, and W. S. Johnson, "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 261.

Dimethyl 1-Chloro-1,3-cyclobutanedicarboxylate. In a 500-ml, three-necked flask equipped with an efficient condenser and mechanical stirrer was placed 28.1 g (0.2 mol) of 1-chloro-1,3-cyclobutanedicarbonitrile and 250 ml of methanol. Hydrogen chloride gas was bubbled into the stirred solution *via* a gas dispersion tube. The reaction was exothermic and the mixture soon began to reflux. The addition of gaseous HCl was continued until the reflux rate slowed. A check by gc showed that no starting material was left and that two isomers of the product had formed with no apparent side products. The mixture was filtered to remove the ammonium chloride and the filtrate was evaporated. The residue was diluted with ether and washed with 5% sodium carbonate and then water. The ether layer was dried, filtered, and evaporated. The residue was distilled to give 27.6 g (67%) of colorless liquid, bp 63–67° (0.2 mm).

Anal. Calcd for $C_8H_{11}ClO_4$: C, 46.50; H, 5.37; Cl, 17.16. Found: C, 46.76; H, 5.50; Cl, 17.16.

Methyl 3-Hydroxy-3-phenyl-1-cyclobutanecarboxylate and Methyl 3-Chloro-3-phenyl-1-cyclobutanecarboxylate. A solution of 53 g (0.276 mol) of 3-hydroxy-3-phenylcyclobutanecarboxylic acid and 1.0 g of *p*-toluenesulfonic acid in 107 g of 2,2-dimethoxypropane and 23 ml of methanol was stirred at room temperature for 24 hr. The volatiles were then removed under reduced pressure leaving the ester as an oil. The oil was not purified further, but was converted directly to 3-chloro-3-phenyl-1-carbomethoxycyclobutane by shaking with concentrated hydrochloric acid.

The oil obtained above was taken up in 100 ml of benzene, and 50 ml of hexane was added. This solution was shaken vigorously for 3 min with 300 ml of concentrated hydrochloric acid. The layers were separated, and the aqueous phase was extracted with two portions of benzene. The combined organic phase was washed twice with cold water, and twice with brine, and then dried over magnesium sulfate. Removal of solvent under reduced pressure gave methyl 3-chloro-3-phenyl-1-cyclobutanecarboxylate as a white solid, mp 83–85°. The product obtained here was the same as that obtained by treatment of 3-chloro-3-phenylcyclobutanecarboxylic acid with diazomethane: nmr ($CDCl_3$) δ 7.32 broad singlet (5 H), 3.4–3.9 $-OCH_3$ singlet and α-H (4 H), 2.8–3.2 broad doublet (4 H). *Anal.* Calcd for $C_{12}H_{13}O_2Cl$: C, 64.13; H, 5.83; Cl, 15.78. Found: C, 64.20, 64.31; H, 5.94; 5.92; Cl, 15.52.

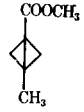
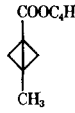
Representative Bicyclobutane Synthesis. 1-Methylbicyclobutanecarboxylate. In a 2-l., four-necked flask fitted with motor-driven stirrer, thermometer, and reflux condenser fitted with a nitrogen T was placed 20.0 g of a 54% dispersion of sodium hydride in mineral oil (0.448 mol). Pentane, 200 ml, was added with stirring and, now containing the mineral oil, was removed with a suction frit. The process was repeated, and the clean sodium hydride was covered with 400 ml of tetrahydrofuran containing 0.3 g of di-*tert*-butylquinone. The suction tube was replaced by a dropping funnel and the condenser was connected to a wet test meter. About 15 ml of a solution of 63.0 g (0.424 mol) of methyl 3-chlorocyclobutanecarboxylate in 100 ml of tetrahydrofuran was added with stirring and the mixture was warmed to 45–50° at which temperature hydrogen began to be evolved. If it were not, 5–10 ml of *N*-methylpyrrolidone was added which usually initiated reaction. If still no reaction occurred, a little ethylene bromide was added. After the induction period was over, the heating bath was removed and the addition was continued at a rate which maintained the temperature at 45–50° and gave a smooth evolution of hydrogen. The addition was complete in ~30 min and hydrogen evolution ceased after an additional 50 min to give a total of 10.9 l. of gas.

The mixture was chilled with an ice bath and 64 ml of saturated potassium chloride solution was added cautiously. The tetrahydrofuran layer was decanted from a heavy sludge of salts which was washed thoroughly with tetrahydrofuran. The combined organic layers were back-washed with 50 ml of saturated aqueous potassium chloride solution. The organic layer was dried, concentrated, and distilled to give 35.7 g (75.1%) yield of methyl bicyclobutane-1-carboxylate, bp 60–62° (36 mm) (lit.[3b] bp 39–42° (12 mm)). Characterization of this and other bicyclobutane esters is given in Table V. In general, cis–trans mixtures of the 3-halocyclobutane derivatives were employed and both components reacted satisfactorily. The order of solvent effectiveness was: ether < THF < *N*-methylpyrrolidone.

Dimethyl-1-[3-phenylbicyclo[1.1.0]butyl]methanol. To a cold (−5°) solution of 25 ml of ethereal methyllithium (0.042 mol) and 50 ml of THF was added under nitrogen a solution of 3.57 g (0.019 mol) of methyl 3-phenyl-1-bicyclobutanecarboxylate in 50 ml of THF. After addition was complete (1 hr), the solution was stirred at 25° for 2 hr. The solution was then cooled in an ice bath and 60 ml of methanol was added. The mixture was poured onto 1 l. of water, which was then extracted with ether. The ether was in turn extracted twice with water and brine and then dried over magnesium sulfate. Removal of solvent gave a solid which was recrystallized from hexane to give 2.3 g of product: mp 64–65°; ir (KBr) 3.05, 3.29, 3.35, 3.42, 6.24, 6.37, 6.73, 8.69, 13.08, 13.14, 14.42 μ; uv $\lambda_{max}^{cyclohexane}$ 275 mμ (13,100). The accuracy of the extinction coefficient is questionable since the spectrum changed with time. The reason for this is not yet known (nmr (CCl_4) δ 7.14 singlet (5 H), 2.19 singlet (2 exo H), 1.43 singlet (1 H, OH) 1.10 singlet (6 H) 0.87 singlet (2 endo H). *Anal.* Calcd for $C_{13}H_{16}O$: C, 82.90; H, 8.57. Found: C, 83.16; H, 8.63).

Bicyclobutane-1-carboxylic Acid. A mixture of 7.0 g (0.0625 mol) of methyl 1-bicyclobutanecarboxylate and 11.0 ml of 5.0 *N* aqueous sodium hydroxide solution (0.066 mol) was stirred magnetically under N_2 for 2.0 hr. Traces of di-*tert*-butylquinone and

Table V. Preparations of Bicyclobutane Esters

Bicyclobutane ester	Mol of chloro ester	Solvent	Base	Temp, °C	Time, hr	Yield of BB, %	Bp (mm) or mp, °C	Gc purity, %	Analysis, %	Ir	Nmr
	1.4	THF	NaH	28	16	82	66 (25)	99+	$C_7H_{10}O_2$: C, 66.64; H, 7.99 Found: C, 66.95; H, 8.25	3.36 (s) (CH), 5.83 (s) (ester C=O), 7.26 (m) (CH_3) 8–9 (s) (C—O)	τ 6.33 (s, 3, methoxyl), 7.83 (s, 2, exo), 8.50 (s, 3, methyl), 8.79 (s, 2, endo)
	0.7	THF	KOC_4H_9-*tert*	0–28	1.8	80	85–86 (32)	99	$C_{10}H_{16}O_2$: C, 71.39; H, 9.59 Found: C, 71.11; H, 9.76	3.35 (s) (CH), 5.86 (s) (ester C=O), 7.12 (m), 7.26 (m), 7.31 (m) (CH_3), 8.47 (s) (C—O)	τ 7.92 (s, 2, exo), 8.49 (s, 3, methyl), 8.57 (s, 9, *tert*-butyl), 8.88 (s, 2, endo)
	0.16	THF	NaH	55	3.4	46	Below 30 (0.3)		$C_9H_{14}O_2$: C, 70.10; H, 9.15 Found: C, 70.16, 70.10; H, 9.35, 9.44	3.21 (w), 3.26 (m), 3.36 (s) (CH), 5.83 (s) (ester C=O), 7.16, (m), 7.33 (m) (methyl)	τ 7.74 (m, 2, exo), 8.03 (m, 1, bridgehead) 8.58 (s, 9, *tert*-butyl), 8.97 (m, 2, endo)
	0.54	THF	NaH	55	2.3	61	32–34 (0.35)		$C_{10}H_{16}O_2$: C, 71.39; H, 9.59 Found: C, 70.34, 70.61, 70.62; H, 9.16, 9.76, 9.33	3.21 (w), 3.26 (w), 3.39 (m), 3.45 (sh), (CH), 5.83 (s) (ester C=O)	τ 6.37 (s, 2, OCH_2) 7.81 (m, 2 exo) 8.10 (p, 1, bridgehead), 9.06 (m, 2, endo), 9.20 (s, 9, *tert*-butyl)
	See text									3.23 (w), 3.35 (m), 3.40 (s), 3.48 (m) (CH), 5.86 (s) (ester C=O) 8–9 (s) (C—O)	τ 6.51 (s, 3, methoxyl), 7.88 (m, 3, bridgehead and exo), 9.04 (m, 2, endo)
	0.0513	THF	NaH	25	16	89.7 not recrystd	Mp 67–68		$C_{12}H_{12}O_2$: C, 76.57; H, 6.43 Found: C, 76.62; H, 6.47	5.86 μ (s) (ester C=O) Uv: λ_{max} (cyclohexane) 252 mμ (13,200)	τ 2.80 (s, 5, aromatic) 6.63 (s, 3, OCH_3) 7.17 (t, 2, exo) 8.50 (t, 2, endo)
	0.13	THF	NaH	45	1.5	61.2	Crystalline sublimed at 63 (0.4)				τ 6.30 (s, 6, methoxyl), 7.09 (m, 2, exo), 8.05 (m, 2, endo)

phenothiazine were present. At the end of this time most of the ester had dissolved. Avoiding air as much as conveniently possible, the mixture was washed with 50 ml of ether, chilled, and poured into a cold well-stirred mixture of 50 ml of 1.5 *N* sulfuric acid and 50 ml of ether. The mixture was shaken well. The water layer was separated and extracted with 50 ml of ether. The combined ether layers were washed with 10 ml of saturated aqueous KCl solution, dried over $MgSO_4$, filtered under N_2, and rotary evaporated at room temperature. The oily residue crystallized when evacuated briefly to 0.5 mm. The crude acid was purified by dissolving it in 50 ml of pentane, shaking well, decanting, and rotary evaporation. Final purification was accomplished by crystallization from 30 ml of pentane at −80°, rapid filtration under N_2, and brief drying at 0.5 mm. The crystalline white solid, 1.59 g (26%), melted at ~51° and then polymerized: ir 2.8–3.6 (broad) (OH of acid) 5.85 μ (>C=O of acid).

Anal. Calcd for $C_5H_6O_2$: C, 61.21; H, 6.17; neut equiv 98.1. Found: C, 60.88, 61.15; H, 6.44, 6.57; neut equiv 100.5.

1-Bicyclobutanecarboxamide. In a 500-ml erlenmeyer flask with magnetic stirrer were placed 23.7 g (0.3 mol) of 1-bicyclobutanecarbonitrile, 200 ml of absolute ethanol, 10 ml of 6 *N* sodium hydroxide solution, and 50 ml of 30% hydrogen peroxide solution. The reaction became exothermic (peak temperature ~55°). The mixture was stirred for ~1 hr and then filtered to remove a small amount of white solid. The filtrate was evaporated under reduced pressure and the residue was recrystallized from 400 ml of boiling ethyl acetate to give 8.0 g (27%) of lustrous white crystals. A recrystallization from ethyl acetate afforded 6.3 g of product and 1 g of insoluble white polymer, inherent viscosity = 0.71 (0.1% in formic acid at 25°).

The recrystallized amide did not melt cleanly, but softened somewhat with polymerization at ~135°: ir 2.98 and 3.13 ($-NH_2$), 3.37 (saturated C–H), 6.03 and 6.17 μ ($-CONH_2$); nmr (DMSO-d_6) δ 0.86 (m, 2 H, endo H's), 1.98 (m, 1 H, bridgehead H), 2.21 (m, 2 H, exo H's), and 6.9 (broad, 2 H, $-NH_2$).

Anal. Calcd for C_5H_7NO: C, 61.84; H, 7.27; N, 14.42; mol wt 97. Found: C, 61.31, 61.12; H, 7.29, 7.35; N, 14.44, 14.25; mol wt (mass spectrum) 97.

3-Acetylcyclobutanol. To a solution of 105 g (1.08 mol) of 3-hydroxycyclobutanecarbonitrile in 1200 ml of anhydrous THF was added 830 ml of 3 *M* methylmagnesium bromide in ether at such a rate as to maintain gentle reflux. After the addition of the Grignard reagent the reaction mixture was heated under reflux for 18 hr. The mixture was then hydrolyzed with 6 *N* HCl and the organic layer separated. The aqueous layer was continuously extracted for 24 hr with chloroform. The extracts were combined and dried briefly over anhydrous potassium carbonate and then over anhydrous sodium sulfate. The solvent was evaporated and the residue (113 g) was distilled under reduced pressure. There was obtained 70 g (47%) of 3-acetylcyclobutanol, bp 67° (0.1 mm).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83; mol wt, 114. Found: C, 63.02; H, 9.01; mass spectrum parent ion *m/e* 114.

3-Iodo-1-acetylcyclobutane. To a cold (0–5°) solution of 38.1 g (0.33 mol) of 3-acetylcyclobutanol and 29 g (0.36 mol) of dry pyridine in 100 ml of chloroform was added a cold (0–5°) solution of 58.9 g of benzenesulfonyl chloride in 100 ml of chloroform. The mixture was stirred and kept cold with an ice–water bath for 2.5 hr and then allowed to warm to room temperature overnight. The reaction mixture was washed with 100 ml of cold 3 *N* HCl, then with 100 ml of water, and finally with 100 ml of saturated sodium bicarbonate. The solution was dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure to give 84.8 g of 3-acetylcyclobutyl benzenesulfonate.

A mixture of 69.3 g of 3-acetylcyclobutyl benzenesulfonate and 81.8 g (0.54 mol) of sodium iodide in 400 ml of dry acetone was stirred and heated under reflux for 48 hr. The cooled mixture was filtered and the salt washed with acetone. The filtrate was then evaporated and the residue diluted with 500 ml of water and the entire mixture extracted with ether. The dark ether extract was washed with aqueous sodium bisulfite until colorless and finally washed with water. After the extract was dried over anhydrous sodium sulfate, the solvent was evaporated to give 61 g of crude product. This was distilled under reduced pressure through a spinning-band column to give 48 g (76% yield from 3-acetylcyclobutanol) of 3-acetylcyclobutyl iodide as a colorless liquid, bp 46–47° (0.1 mm). This mixture of cis and trans isomers slowly turns dark on standing or on exposure to air and light.

Anal. Calcd for C_6H_9IO: C, 32.00; H, 4.05; I, 56.50; mol wt 224. Found: C, 31.48, 31.39; H, 4.38, 4.36; I, 55.51; mol wt 218 (cryoscopic).

1-Acetylbicyclobutane. To a 2-l. three-necked flask equipped with a dropping funnel, mechanical stirrer, and condenser was added 14.3 g of 54% sodium hydride in mineral oil. The mineral oil was removed with two 150-ml portions of dry pentane. To the mineral oil free sodium hydride was then added 500 ml of anhydrous THF. To this stirred suspension of sodium hydride in THF was added dropwise from the dropping funnel 72.8 g (0.325 mol) of 3-acetylcyclobutyl iodide. Occasional cooling with an external cold water bath was necessary to keep the temperature below 35°. The reaction mixture was stirred for 2–3 hr after all the iodide was added or until 90–95% of the calculated amount of hydrogen was evolved. Phenothiazine (0.1 g) was added and the mixture was filtered through a pad of Celite to remove unreacted NaH and sodium iodide. The light yellow solution was shaken with 200 ml of saturated aqueous sodium chloride. The aqueous phase was separated and extracted with two 150-ml portions of ether. The combined organic extracts were dried over anhydrous sodium sulfate. This mixture was filtered and the solvent distilled through a short column. Near the end of the distillation the pressure was reduced to remove the last trace of solvent. The residue was evaporatively distilled at approximately 1 mm into a gas trap cooled in Dry Ice–acetone to give 18 g (57.5%) of 1-acetylbicyclobutane as a crystalline solid, mp −23°, bp 39° (8 mm). 1-Acetylbicyclobutane polymerizes rapidly in the liquid phase without an inhibitor. ^1H nmr (CCl_4) (2) *exo*-bicyclobutyl protons as a doublet (each split again) at δ 2.38 ppm, (1) bridgehead multiplet overlapping with a sharp singlet (3, C (=O) CH_3), and (2) *endo*-bicyclobutyl protons as a doublet (each split again) at 1.10; ir λ_{max} 3.38, 6.00, 6.65, 7.13, 8.35, 8.80, 10.40, 11.95 μ; mass spectrum *m/e* parent ion at 106.

Phenyl 3-Methylenecyclobutyl Ketone. To a stirred solution of 9.3 g (0.1 mol) of 3-methylenecyclobutanecarbonitrile in 100 ml of ether was added a solution of 50 ml of 3 *M* phenylmagnesium bromide in 150 ml of ether. This mixture was heated under reflux for 2 hr and then poured into 200 ml of cold 6 *N* hydrochloric acid and stirred for 30 min. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was distilled off leaving 15.0 g (87%) of the product as a slightly yellow oil. This material was distilled under reduced pressure to give phenyl 3-methylenecyclobutyl ketone as a colorless oil: bp 70–74° (0.15 mm); ir λ_{max} 5.95 (C=O), 11.40 μ (>=CH_2); uv $\lambda_{max}^{cyclohexane}$ 241 (ε 14,000) 278 (894), 287 (735), 321 (61), and 328 mμ (61); ^1Hnmr (CCl_4) (5) aromatic protons as a multiplet at δ 7.90 and 7.40, (2) exo vinylic protons as a multiplet at 4.80, (1) cyclobutyl proton as a pentuplet centered at 3.82, (4) cyclobutyl methylene protons as a multiplet at 2.90 ppm.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02; mol wt 172. Found: C, 83.69; H, 7.23.

A 2,4-dinitrophenylhydrazone derivative was prepared and an analytical sample recrystallized from 95% ethanol, mp 119–121°.

Anal. Calcd for $C_{18}H_{14}N_4O_4$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.63, 61.63; H, 4.50, 4.59; N, 15.81.

3-Methyl-1-benzoylbicyclobutane. From 25.6 g of phenyl 3-methylene cyclobutyl ketone and 150 ml of 55% hydroiodic acid there was obtained 54.2 g of crude phenyl 3-iodo-3-methylbicyclo[1.1.0]butyl ketone. A mixture of 7.5 g of 54.3% NaH in mineral oil (the mineral oil was removed with dry pentane), 180 ml of ether, and 54 g of phenyl 3-iodo-3-methylcyclobutyl ketone was stirred under an atmosphere of nitrogen for 36 hr. The reaction mixture was filtered and the solids washed with a little ether. The filtrate was washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure leaving 18 g of a light yellow oil, which was distilled through a spinning-band column under reduced pressure. There was obtained 10 g (39%) of phenyl 3-methylbicyclo[1.1.0]butyl ketone as a slightly yellow oil: ir λ_{max} 3.30, 3.40, 6.13, 6.26, 6.35, 7.30, 7.55, 8.30, 10.00, 10.15, 13.85, and 14.35 μ; uv $\lambda_{max}^{CH_3CN}$ 243 (ε 7150), sh 280 mμ (1090); mass spectrum *m/e* parent ion 172; ^1Hnmr: (5) aromatic protons as multiplets centered at δ 7.85 and 7.35, (2) *exo*-bicyclo[1.1.0]-butyl protons as a triplet at 2.35, (2) *endo*-bicyclo[1.1.0]butyl protons as a triplet at 1.43, and (3) methyl protons as a sharp singlet at 1.33 ppm.

1,3-Dichloro-1-methylcyclobutane. A 5-l., three-necked flask equipped with a mechanical stirrer and two long, wide-bore condensers was charged with 1 l. of benzene, 225 g (0.51 mol) of lead tetraacetate (dried by evacuation at the pump), 30 g (0.71 mol) of lithium chloride, and 75.5 g (0.51 mol) of 3-methyl-3-chlorocyclobutanecarboxylic acid. The system was swept with nitrogen. The mixture was heated to gentle reflux, and gas was vigorously evolved. It was sometimes necessary to remove the mantle hurriedly until the reaction subsided. After the initial reaction sub-

sided, the mixture was refluxed until the benzene layer was colorless or until a small portion gave no brown precipitate with water (about 1 hr). The mixture was cooled, and 800 ml of distilled water was added to dissolve the sticky inorganic phase. The organic layer was washed with three 400-ml portions of water and one 50-ml portion of sodium bicarbonate solution, and finally with 400 ml of water. The solution was dried over magnesium sulfate and filtered, and the benzene was distilled through a large glass helices packed column. The residue was distilled in a small wire spiral column to give 30.3 g (0.218 mol, 43%) of the dichloride, bp 131.5–141.5°. If distilled at atmospheric pressure, the dichloride yellows on standing; it is best distilled at about 137 mm (bp 80–90°).

The reaction can be carried out on a 1-mol scale using a 12-l. flask equipped with three condensers. A temperature of 65–70° was found to give a more controlled rate of gas evolution.

1-Methylbicyclobutane. A 1-l. three-necked flask equipped with a small wire spiral still, dropping funnel, magnetic stirrer, and heating mantle was dried by flaming under a stream of nitrogen. For larger runs a mechanical stirrer was found to be necessary. The cooled flask was then charged with 325 ml of dioxane (spectrograde, distilled from sodium) and 25 g (1.1 mol) of sodium metal. The system was swept with nitrogen, and the flask was heated until the dioxane refluxed at the bottom of the still. A solution of 30 g (0.216 mol) of 1,3-dichloro-1-methylcyclobutane in 45 ml of dioxane was added over 1.3 hr. The reaction was exothermic, requiring modification of the Variac setting controlling the mantle during addition. As the dichloride was added, the hydrocarbon formed and distilled, bp 35–45°. To maintain the sodium in a molten state (pot temperature of 98°), the head temperature reached 85°, and the product distilled from the pot rather sporadically. The heating was continued for 1 hr after the addition was complete, and finally the flask was heated until the dioxane reached the still head. The distillate was redistilled through the wire spiral column to give 12.1 g (0.178 mol, 82%) of the product, bp 32.5–34.5°. The nmr (neat) shows δ 0.46 singlet (2-H's), 1.0 multiplet (1-H), 1.28 doublet (2-H's), and 1.55 (3-H's).

2,2,4,4-Tetramethyl-1,1,3,3-tetrachlorocyclobutane. This compound was prepared by the procedure of Gilch[10] modified in that the crude solid was heated on the steam bath and stirred for 1 hr with 7% sodium hydroxide solution. The mixture was cooled, and the solid was filtered, washed thoroughly with water, and dried. The product was obtained in 87.3% yield and melted at 236–237.5° (lit.[10] mp 236°). The purity as determined by gas chromatography was greater than 99%: nmr τ 8.46 (s).

Reduction of 2,2,4,4-Tetramethyl-1,1,3,3-tetrachlorocyclobutane with Tributyltin Hydride. A mixture of 77.8 g (0.311 mol) of the tetrachloride and 500 ml of benzene was heated to reflux. Azobisisobutyronitrile, 0.35 g, was added and then during 85 min was added a solution of 210 g (0.722 mol) of tributyltin hydride in 350 ml of benzene. Additional azo compound was added and the mixture was stirred and refluxed for 2 hr. A final portion, 0.35 g, of azo compound was added and the mixture held at reflux with stirring for 16 hr. It was steam distilled. The aqueous layer was separated and extracted with 100 ml of benzene. The organic layers were dried, and the benzene was distilled in a spinning-band column. Distillation under reduced pressure gave 44.5 g (78.9%) of 2,2,4,4-tetramethyl-1,3-dichlorocyclobutane, bp 84.6–85.5° (32 mm), mp 41–49° (sealed cap).

Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.05; H, 7.79. Found: C, 53.21; H, 7.97.

The mixture consisted of 62.6% of one isomer and 37.0% of the other for an overall purity of 99.6% by gc: nmr (isomer A) τ 6.02 (s, 2, adjacent to Cl), 8.78 (s, 12, methyls); (isomer B) τ 6.19 (s, 2, adjacent to Cl), 8.82 (s, 12, methyls).

The ir spectra were consistent and similar, but B was transparent at 12.71 μ while A absorbed with medium intensity there.

Preparative gc of a forerun, bp 43–47° (25 mm), permitted the isolation of 2,2,4,4-tetramethylcyclobutyl chloride: nmr τ 6.09 (s, 1, adjacent to Cl), 8.35 (two s, 2, methylene), 8.89 (two s, 12, methyls).

Anal. Calcd for $C_8H_{15}Cl$: Cl, 24.17. Found: Cl, 24.06.

Attempted $LiAlH_4$ reduction gave mainly starting material, but a little material of smaller retention time on the preparative gc column was mainly the corresponding 1,1,3-trichloride, mp 102–112°: nmr τ 6.03 (s, 1, adjacent to Cl), 8.62, 8.64 (two s, 12, methyls).

Anal. Calcd for $C_8H_{13}Cl_3$: C, 44.57; H, 6.08. Found: C, 44.53; H, 6.14.

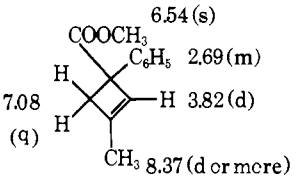
2,2,4,4-Tetramethylbicyclobutane. A 1-l., three-necked flask was fitted with dropping funnel, small spinning-band column, and thermometer. In it were placed 38 g of a 40% dispersion of sodium in mineral oil (0.66 mol) and 375 ml of triglyme (freshly vacuum distilled from sodium). The flask was heated with an oil bath to 120° and a manostat maintained the pressure at 80 mm. A Dry-Ice chilled trap was present in the line. During 30 min, a solution of 32 g (0.176 mol) of 2,2,4,4-tetramethyl-1,3-dichlorocyclobutane in 50 ml of triglyme was dripped in at a rate which maintained the internal temperature at 130–140°. The reaction was moderately exothermic and the mixture turned bright blue. The product distilled at 67–80° (80 mm) into a receiver chilled with ice and methanol. This was combined with the trap contents (10 ml) to give the crude product. Redistillation gave 9.05 g (47%) of pure 2,2,4,4-tetramethylbicyclobutane, bp 104°. On storage at −80°, it crystallized completely: ir 3.28 (ring CH), 3.37, 3.47 (-CH_3), 7.28, 7.40 μ (*gem*-dimethyl); nmr τ 8.76 (6 H, *exo*-CH_3's), 8.95 (6 H, *endo*-CH_3's), 9.05 (2 H, bridgehead H's).

Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 86.20; H, 13.02.

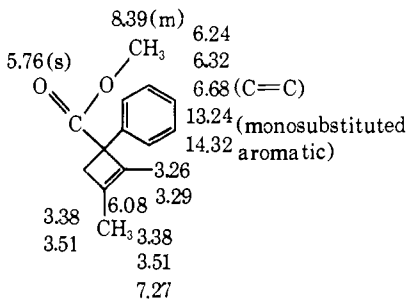
Benzyne Addition to Methyl 3-Methyl-1-bicyclobutanecarboxylate. To a refluxing solution of 8.84 g (0.0702 mol) of methyl 3-methyl-1-bicyclobutanecarboxylate, 9.26 g (0.0788 mol) of isoamyl nitrite, and 80 mg of 2,5-di-*tert*-butylquinone in 200 ml of methylene chloride was added with stirring during 2.5 hr a solution of 10.0 g (0.0728 mol) of anthranilic acid in 55 ml of tetrahydrofuran. The solution became progressively darker during the addition. It was cooled and washed with 500 ml of water containing 10 ml of 37% hydrochloric acid, with 500 ml of water, with 500 ml of water containing 10 g of sodium hydroxide, and with 500 ml of water. It was treated with magnesium sulfate, Darco, and Celite, filtered, evaporated and distilled in a molecular still. The product was 8.84 g (62.3%) of a pale yellow liquid, bp 46–57° (0.18 mm). The fractions seemed inhomogeneous and of slightly different color, yet they possessed almost identical nmr spectra.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 75.92, 76.00; H, 7.17, 7.12.

The color lightened on keeping to a very pale yellow. The nmr assignment was

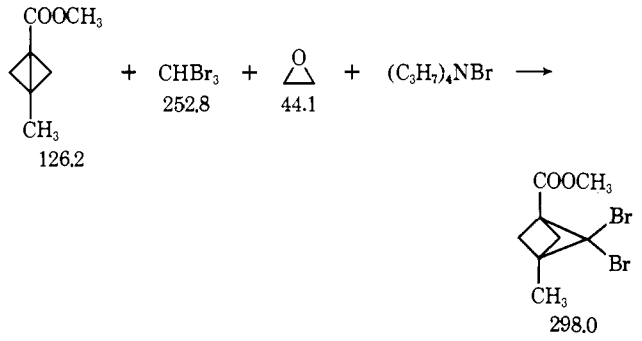


CH_2 appears as AB with further splitting. The vinyl H doublet and the CH_3 are also further split. .



Methyl 2,2-Dichloro-3-methylbicyclo[1.1.1]pentanecarboxylate. A mixture of 12.6 g (0.1 mol) of methyl 3-methyl-1-bicyclobutanecarboxylate, 14.3 g (0.12 mol) of chloroform, 13.5 g (0.31 mol) of ethylene oxide, and 0.3 g of tetrapropylammonium bromide was heated in a stainless steel bomb at 170° for 6 hr during which time the pressure dropped from 245 to 140 psi. The crude product, 56 g, was distilled twice to give a complex mixture of products, bp 42–134° (0.4 mm). Preparative gc of the early cuts, bp 42–78° (0.5 mm), gave 0.65 g of product with retention time 2.7 min: nmr ($CDCl_3$) τ 5.22 (broad s, 2, syn), 6.27 (s, 3, methoxyl), 6.80 (broad s, 2, anti), 8.27 (s, 3, methyl); ir 3.25 (w, 3.37 (m), 3.47 (sh) (CH), 5.76 (s) (C=O), 6.03 (m), 6.21 (m) (unknown), 7.25 (s) (methyl).

Methyl 2,2-Dibromo-3-methylbicyclo[1.1.1]pentanecarboxylate. A mixture of 12.6 g (0.1 mol) of methyl 3-methyl-1-bicyclobutanecarboxylate, 21.1 g (0.12 mol) of bromoform, 13.5 g (0.31 mol) of ethylene oxide, and 0.3 g of tetrapropylammonium bromide was heated in a stainless steel bomb at 150° for 4 hr during which time



the pressure dropped from 190 to 30 psi. The crude product was received as 44 g of nonvolatile liquid. Two distillations yielded 9.71 g of liquid in four fractions, bp 61–90° (0.15 mm). Preparative gc of the two early cuts, bp 61–67° (0.15 mm), gave 1.4 g with retention time 15.3 min.

Anal. Calcd for $C_8H_{10}O_2Br_2$: C, 32.40; H, 3.42. Found: C, 32.37; H, 3.60.

The nmr and ir spectra were identical with that of the dichloro derivative within experimental error. As for the dichloride, the ir spectrum showed apparent C=C but either this is characteristic for the bicyclo[1.1.1]pentanes or a trace of intensely absorbing cyclobutene, undetected by nmr, is present.

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Bicyclo[1.1.0]butanes from Ketene and Vinyl Ethers

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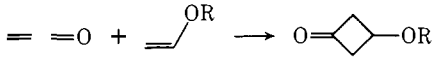
Abstract: Four 3-alkoxycyclobutanones were prepared from ketene and vinyl ethers. Five bicyclobutanes, **4**, **7**, **12**, **16**, and **25**, were prepared from these ketones. The syntheses described provide easy access to large quantities of a variety of bicyclobutanes.

The addition of ketene to vinyl ethers has been known for some time, although the reported yields are not encouraging.[1] We found that ketene undergoes thermal cycloaddition to simple vinyl ethers in yields which are synthetically acceptable. The products of these additions were the expected 3-alkoxycyclobutanones,[1] which are convenient entries into the 1,3-disubstituted cyclobutane series and particularly the bicyclobutane series.

3-Alkoxycyclobutanones. Four vinyl ethers were heated with ketene at 100° for 4 hr in the absence of solvent. The crude reaction mixtures required distil-



R = Me, Et, *tert*-Bu, CH_2Ph

lation as the only purification step. Diketene in varying amounts and about 10% (based on ketene charged) of higher boiling, unidentified material were present in every case. The reactivity of the vinyl ethers toward ketene, as measured by the alkoxycyclobutanone:diketene ratio, was qualitatively in the order R = *tert*-Bu ≫ Et > Me > CH_2Ph. This order corresponds to the relative ability of R to stabilize a partial positive charge on oxygen in the transition state.[2] The 3-alkoxycyclobutanones are suitable intermediates for the preparation of bicyclobutanes, and Scheme I illustrates the generality of the method for the preparation of the hydrocarbon series.

(1) C. D. Hurd and R. D. Kimbrough, Jr., *J. Amer. Chem. Soc.*, **82**, 1373 (1960); J. C. Martin, U. S. Patent, 3,285,915 (1966).

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Scheme I