Upon completion of the addition the reaction was heated at reflux for 0.5 hr., cooled and hydrolyzed first with 100 ml. of water, then with 300 ml. of 6*N* sulfuric acid. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under vacuum. The residue was refluxed with 1 g. of *p*-toluenesulfonic acid at reduced pressure for 2 hr., cooled, redissolved in 200 ml. of ether, and the solution washed first with several 100-ml. portions of 10% aqueous sodium hydroxide, then with several 100-ml. portions of water. After drying the organic layer over anhydrous calcium chloride and removal of the solvent under vacuum, the residue was distilled at reduced pressure to give 39.7 g. (52%) of a colorless liquid, b.p. 84° (7 mm.), n_D^{25} 1.5310 (lit. b.p. 99–100° (15 mm.), n_D^{20} 1.5300, prepared by dehydration of the alcohol over alumina).[26]

A sample of the liquid rapidly absorbed bromine in carbon tetrachloride without evolution of hydrogen bromide gas.

The following absorption bands were observed in the infrared region: 1660 cm.$^{-1}$ (w) and 964 cm.$^{-1}$ (s) which are characteristic of internal olefin. The compound absorbed in the ultraviolet region: $\lambda_{max}^{cyclohexane}$ 250 mμ, ε 16,900.

5-Phenylpentene-1 (IV). The procedure of von Braun[27] was followed. From 5.0 g. (0.2 g.-atom) of magnesium turnings, 40.0 g. (0.22 mole) of β-bromoethylbenzene in 200 ml. of ether and 24.2 g. (0.2 mole) of redistilled allyl bromide was obtained 15.7 g. (53%) of 5-phenylpentene-1, b.p. 70° (6 mm.), n_D^{25} 1.5021 (lit. b.p. 77–78° (10 mm.), n_D^{20} 1.5065).[27]

A sample of the liquid rapidly absorbed bromine in carbon tetrachloride without the evolution of hydrogen bromide gas.

In the infrared region the compound exhibited absorbance which is characteristic of a vinyl olefin: 1645 cm.$^{-1}$ (m), 912 cm.$^{-1}$ (s) and 992 cm.$^{-1}$ (m).

Reduction of 1-nitroso-2-phenylpiperidine with sodium hydrosulfite. In a system equipped for the collection of any evolved gases, a stirred solution of 68.5 g. (0.36 mole) of 1-nitroso-2-phenylpiperidine in 1800 ml. of ethanol and 1500 ml. of 20% aqueous sodium hydroxide was heated under a continuous flow of nitrogen at 60° in an oil bath. In a solids-addition funnel was placed 188 g. (1.1 moles) of powdered sodium hydrosulfite, and the system was closed and allowed to come to equilibrium. The solid sodium hydrosulfite was then added uniformly over a 0.5-hr. period and the reaction stirred at 60° for 10 hr. No gas evolution was observed.

The cooled reaction mixture, containing suspended solid, was extracted with ether in several portions. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and solvent was removed under vacuum. The residue was redissolved in anhydrous ether and treated with hydrogen chloride gas. The resulting voluminous, white precipitate was filtered and recrystallized twice from ethanol giving 25.0 g. (33%) of white solid, m.p. 203–204.5°. A mixture melting point of this material and 1-amino-2-phenylpiperidine hydrochloride obtained by the lithium aluminum hydride reduction of 1-nitroso-2-phenylpiperidine was not depressed.

Acknowledgment. The authors wish to acknowledge gratefully the support of this work by the Hooker Chemical Co. and the National Science Foundation under Grant No. G-5247.

BROOKLYN 1, N. Y.

(26) R. Ya. Levina and N. A. Shchglova, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 527 (1941).

(27) J. v. Braun, H. Deutsch, and A. Schmatloch, *Ber.*, **45**, 1255 (1912).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY AND THE DEPARTMENT OF CHEMISTRY, GRINNELL COLLEGE]

Free Radical Chlorination of Cyclobutanecarboxylic Acids

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Cyclobutanecarboxylic acid, 1,1-cyclobutanedicarboxylic acid, and their respective acid chlorides have been chlorinated with sulfuryl chloride in the presence of benzoyl peroxide. Predominantly *trans* chlorination results with major attack at the 3-position. No product was isolated indicating attack at the tertiary hydrogen present in the monoacid and its acid chloride. A chromatographic technique has been developed which separates the five geometric isomers of monochlorocyclobutanecarboxylic acid.

Most data suggest that free radical chlorination of alipahtic compounds attacks C—H bonds in the order primary < secondary < tertiary.[5] Sulfuryl chloride has shown particular selectivity for tertiary hydrogens in aliphatic systems.[6] However, Brown and Ash[7,8] have shown that with substituted aliphatic chains two factors were most important in the liquid phase free radical chlorination: the inductive effect of a substituent and the stability of the organic free radical intermediate. Moreover, they have shown the action of such inductive groups to be additive. In an attempt to extend these generalizations to alicyclic systems we have investigated the free radical chlorination of cyclobutanecar-

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(2) Abstracted in part from a Ph.D. dissertation, California Institute of Technology, 1954.

(3) Abstracted in part from an Honors dissertation, Grinnell College, 1959.

(4) Abstracted in part from an Honors dissertation, Grinnell College, 1961.

(5) C. Walling, *Free Radicals in Solution*, J. Wiley and Sons, Inc., New York, 1957.

(6) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4031 (1955).

(7) A. B. Ash and H. C. Brown, *Record Chem. Prog.* (*Kresge-Hooker Sci. Lib.*), **9**, 81 (1948).

(8) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955).

TABLE I

DIRECTIVE EFFECTS IN FREE RADICAL CHLORINATION

Compound	Isomer Distribution				Total Yield per Position		
	2-*cis*	2-*trans*	3-*cis*	3-*trans*	1-Cl	2-Cl	3-Cl
n-Butyric acid[a]					10	45	45
n-Butryl chloride[a]					3	49	48
Cyclobutanecarboxylic acid	0	46	12	42	0	46	54
Cyclobutanecarboxylic acid chloride	2	36	26	36	0	38	62
1,1-Cyclobutanedicarboxylic acid	0	0	40	60	0	0	100
1,1-Cyclobutanedicarboxylic acid dichloride	0	0	36	64	0	0	100

[a] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, 62, 926 (1940).

boxylic acid, 1,1-cyclobutane-dicarboxylic acid, and their respective acid chlorides.

Cyclobutanecarboxylic acid has, in addition to six possible secondary radicals, a possible and presumably more stable tertiary intermediate involving the 1- position. The chlorination results predicted by consideration of the inductive effect are here in opposition to those predicted on the assumption that the most stable free radical intermediate determines the product.

Chlorination of cyclobutanecarboxylic acid was carried out in sulfuryl chloride solution in the presence of benzoyl peroxide. Analysis of the fractionated chlorination mixture by a chromatographic method similar to that of Ramsey and Patterson[9] indicated the presence of 46% *trans*-2-chloro acid, 42% *trans*-3-chloro acid, and 12% *cis*-3-chloro acid (*cf.* Table I). There was no indication of chlorination in the 1- position. Although a band corresponding to the position of the *cis*-2-chloro acid was seen on the column, this acid could neither be isolated nor titrated and must, therefore, be present in less than the estimated 2% error in the chromatographic method. That no apparent isomerization had occurred during fractionation was shown by chromatographic analysis of mixtures of the five isomeric monochloro acids after they had been refluxed under simulated distillation conditions.

The cyclobutanecarboxylic acid chloride was chlorinated in a manner identical to that of the parent acid. The chlorinated mixture was hydrolyzed, fractionated to remove unchlorinated acid, and analyzed in the usual manner. Isomerization during the hydrolysis was not considered likely, since the point of attack during the hydrolysis does not involve ring carbons. Although hydrogen chloride is formed during the reaction, it was shown that even under reflux conditions it caused no apparent isomerization. Chlorination results are shown in Table I.

The 1,1-cyclobutanedicarboxylic acid was chlorinated with sulfuryl chloride and benzoyl peroxide while suspended in benzene, decarboxylated to form a mixture of monoacids, fractionated, and chromatographically analyzed. The results are shown in Table I. Isomers appear during the decarboxylation step. Thus only the position and not the configurational distribution is due to chlorination. The greater yield of 3-*trans*-chloro acid supports the structure assignment of this compound.

From the work of Ash and Brown[7] one might expect that the free radical chlorination of 1,1-cyclobutanedicarboxylic acid dichloride would provide a mixture of 2-chloro diacid and 3-chloro diacid.[10] It was found in actual practice that the chlorination mixture resulting from sulfuryl chloride and benzoyl peroxide treatment consisted entirely of the 3-chloro-1,1-cyclobutanedicarboxylic acid dichloride, as shown by comparison of the decarboxylation products with authentic materials.

The data of Table I suggest that the inductive effect is an even more important factor in free radical chlorine attack of a cyclobutane ring than in the aliphatic series. Like the aliphatic series, the effects seem to be additive. The reported[5] selectivity of the sulfuryl chloride for tertiary hydrogens is not observed in the alicyclic system. Nevertheless, its size does seem to direct the attack: $SO_2Cl_2 + R\cdot = RCl + \cdot SO_2Cl$ so that the approach is on the opposite side from the carboxyl or acid chloride group (*i.e.*, in a *trans* fashion).

Synthesis and characterization of the monochlorocyclobutanecarboxylic acids. Until this study only one monochlorocyclobutanecarboxylic acid had been produced. The acid, *trans*-3-chlorocyclobutanecarboxylic acid was obtained by R. C. Jones[11] from the rather inaccessible 3-hydroxy-1,1-cyclobutanedicarboxylic acid. Accordingly, necessary to this study was the synthesis and characterization of the possible products of the chlorination, the five isomeric monochlorocyclobutanecarboxylic acids.

The 1-chlorocyclobutanecarboxylic acid may best be prepared from the corresponding monocarboxylic acid through chlorination of the acid chloride, conversion to the methyl ester and hydrolysis:

(9) L. L. Ramsey and W. I. Patterson, *J. Assoc. Offic. Agr. Chemists*, 31, 441 (1948).

(10) However, Professor H. C. Brown predicted, in a private communication, that the 3-chloro diacid and only negligible amounts of 2-chloro diacid would result from the chlorination of 1,1-cyclobutanedicarboxylic acid.

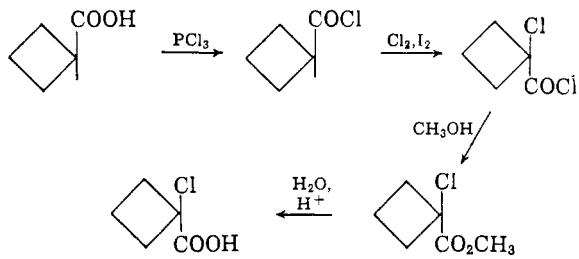
(11) R. C. Jones, Harvard University, Ph.D. thesis, 1941.

TABLE II

BEHAVIOR OF THE MONOCHLOROCYCLOBUTANECARBOXYLIC ACIDS INDICATIVE OF STRUCTURE

Compound	M.P. or B.P.	Rate of Movement on Column	Analysis after 180° 30 Min. in 12*M* HCl	Dipole Moment (× 10^{18}), 25°, Dioxane		
				Acid	Methyl ester	Nitrile
cis-2-acid	97–98.5	slow	80% *trans*, 20% *cis*	2.08	2.40	4.41
trans-2-acid	120–122.5/ 14 mm.	fast	ca. 100% *trans*	2.44	1.51	3.52
cis-3-acid	43.8–45.5	slow	22% *trans*, 78% *cis*	1.68[a]	2.86	2.92
trans-3-acid	51–52.2	fast	47% *trans*, 53% *cis*	1.09[a]	2.61	2.15

[a] *n*-Hexane solution.



Direct conversion of the acid to the 1-chloro acid chloride by the Hell-Volhard-Zelinsky method was not satisfactory, yielding a complex polychlorinated mixture. Monochlorination was achieved by regulating the flow of chlorine through the acid chloride in the presence of iodine at 100°.[12] Treatment of the resulting 1-chloro acid chloride with water yielded a mixture which, on analysis, gave high carbon values, presumably due to anhydride formation. Therefore, the acid chloride was treated with absolute methanol and the methyl ester subjected to acid hydrolysis.

Addition of anhydrous hydrogen chloride to cyclobutenecarboxylic acid[13] led to a mixture of 2-chlorocyclobutanecarboxylic acids. These acids were separated by our chromatographic method and shown by analysis to be 65% of a solid, m.p. 97–98.5° and 35% of a liquid, b.p. 120–122.5°/14 mm.

Configurations of the 2-chlorocyclobutanecarboxylic acids have been deduced on the basis of the data shown in Table II. The liquid acid did not isomerize when treated with concentrated hydrochloric acid in a sealed tube at 180° for thirty minutes. Eighty per cent of the solid acid was converted to the liquid acid under these conditions. Accordingly, the liquid acid may be assigned the *trans* configuration and the solid designated the *cis* isomer. The dipole moments of the acids in dioxane solution are in conflict with the isomerization data. Misleading values would be obtained if solute-solute or solute-solvent complexes exist. The cryoscopic method of evaluating the van't Hoff factor shows both the *cis*-acid (i = 0.9839) and the *trans*-acid (i = 0.9912) to exhibit but little solute-solute association. Similar results have been reported concerning aliphatic acids.[14] Thus it appears that a solute-solvent complex exists. Such complexes are reported for the dicarboxylic acid series.[15] To avoid solute-solvent complexes one may esterify the carboxyl group or convert it to the nitrile.[16] Both the ester and nitrile were prepared according to the following scheme:

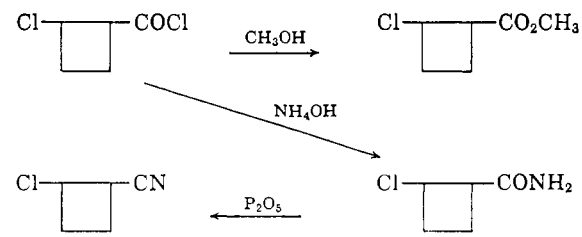


Table II shows that the dipole moments of these compounds are in agreement with the isomerization data. The indicated assignment seems justified.

It should be noted that the assignment of the *cis* configuration to the major product of the hydrohalogenation of cyclobutenecarboxylic acid implies "trans" addition to the double bond and might suggest a mechanism in which the acid group does not directly participate. Such a mechanism has been proposed for hydrogen halide addition to cyclohexenecarboxylic acid.[17] The presence of 35% of the *trans*-acid in our reaction mixture would lead one to question this mechanism since it has been shown in the laboratory that no appreciable conversion of our *cis*-acid into *trans*-acid takes place under hydrohalogenation conditions. It seems more likely that the reaction proceeds by 1,4-addition to give an enol common to each acid. This enol then rearranges in a stereoselective manner:

(12) W. Markownikoff, *Ann.*, **153**, 240 (1870).

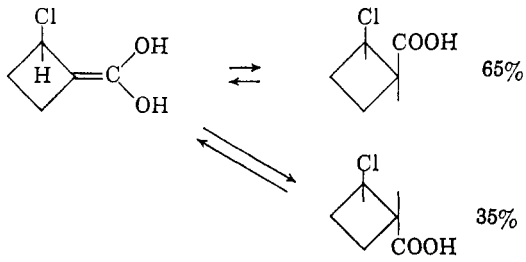
(13) N. A. Domnin and I. P. Yakovlev, *J. Gen. Chem. (U.S.S.R.)*, **17**, 1899 (1947).

(14) R. S. Phadke, *J. Indian Inst. Sci.*, **35A**, 123 (1953).

(15) von Cl. Beguin and T. Gaumann, *Helv. Chem. Acta*, **41**, 1376 (1958).

(16) We are indebted to Professor J. D. Roberts for this latter suggestion.

(17) W. R. Vaughn, R. L. Craven, R. Q. Little, Jr., and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **77**, 1594 (1955).



The rearrangement of an enol is usually considered a solvent assisted step. If this is the present situation then the stereoselectivity observed may be rationalized. The solvent assisted movement of the proton toward the side of the double bond already occupied by the chlorine should be (and apparently is) more hindered than that movement which would produce the *cis*-acid as a major product.

The preparation of the 3-chlorocyclobutanecarboxylic acid mixture *via* the acid dichloride has been mentioned above. Chromatographic analysis indicated that 64% of the monochlorinated material was an acid identical to the 3-chloro acid obtained by Jones,[11] m.p. 51–52.2°. The remaining 36% proved to be a second acid, m.p. 43.8–45.5°.

On the basis of the data of Table II the higher melting acid has been assigned the *trans* configuration; the other acid is thus the *cis*. The dipole moment data are the most convincing in this series. The *cis* acid, ester, and nitrile each show a higher dipole than the corresponding *trans* compounds. These acids, unlike the *cis*-2-chloro acid, show appreciable solubility in the noncomplexing solvent *n*-hexane. Accordingly, dipole measurements were taken in *n*-hexane and solvent-solute association problems did not arise. The isomerization data suggests that there is an equilibrium position for this pair that is near 40 : 60 *cis:trans*. Finally, it may be noted that this assignment is in agreement with the relative movement of these acids on the chromatographic column. Olefinic compounds have shown selective movement on chromatographic columns.[18] Thus it is likely that the 2-chloro acid, m.p. 97–98.5°, and the 3-chloro acid, m.p.43.8–45.5°, have the same configuration.

EXPERIMENTAL[19]

Diethyl 1,1-cyclobutanedicarboxylate. The method employed is essentially that of Cason and Allen[20] as modified by Lemaire[21] to remove allyl malonic ester (b.p. 93°/6 mm.). The ester fraction boiling 100–125°/15 mm. was treated with bromine until an added 1 ml. was no longer immediately decolorized. The resulting amber liquid was fractionated through an electrically heated 15 cm. column packed with 3 mm. glass helices. The portion of b.p. 108–114°/15 mm., n_D^{25} 1.4343 represented a 55.5% yield based on 1,3-dibromopropane.

1,1-Cyclobutanedicarboxylic acid. To an ice cooled solution of 225 g. (4 moles) of ethanolic potassium hydroxide was slowly added 200 g. (1 mole) of diethyl 1,1-cyclobutanedicarboxylate. The white, pasty product was placed on a steam bath for 1.5 hr., with occasional stirring. The salt was filtered by means of a sintered glass funnel, washed with 500-ml. portions of absolute ethanol, and then absolute ether, and air-dried to constant weight. The dry solid was taken up in a minimum amount of water, treated with 300 ml. of concentrated hydrochloric acid and the resulting precipitate removed. The filtrate was evaporated nearly to dryness at 44–50° under an aspirator vacuum. The resulting mush was shaken with 500 ml. of ether, filtered, and the ethereal filtrate evaporated as before until mixing lines in the distillate were observed. The residue was crystallized from 200 ml. of ethylene dichloride and the solid acid was separated from the two-phase mother liquor at about 0°. The air-dried product weighed 102.8 g. (71.3%); m.p. 154–155 dec. One recrystallization raised the decomposition point to 157–158.5°.

Cyclobutanecarboxylic acid. This acid may be produced in 85% yield from the 1,1-cyclobutanedicarboxylic acid. However, it is more conveniently prepared in the usual manner[20] from the diester without the isolation of the diacid.

Cyclobutanecarboxylic acid chloride.[22] Phosphorus trichloride (30.5 g., 0.222 mole, 100% excess) was added dropwise to 33.4 g. (0.334 mole) of cyclobutanecarboxylic acid over a period of 20 min. and then the temperature was raised to 105 ± 5° for 1 hr. The light yellow liquid was then decanted from the more viscous residue and the latter was rinsed with a few ml. of phosphorus trichloride. The bulk of the material and the washing were combined and fractionated. The acid chloride was collected at 65–69°/60 mm. and weighed 30.2 g. (76.2%).

Methyl 1-chlorocyclobutanecarboxylate. A 100 ml., round-bottomed flask, equipped with an inlet tube sealed onto its bottom with a sintered glass disk at the point of attachment, was equipped with a reflux condenser protected by a calcium chloride drying tube. A small positive pressure of air was applied to the inlet tube and 25 g. (0.21 mole) of cyclobutanecarboxylic acid chloride and 0.05 g. of iodine were added to the flask. With the aid of an oil bath, the flask was heated to about 105° and the air pressure was replaced by a flow of chlorine (rate 1.6 g./hr.) until a 20% excess of chlorine has been added. This crude mixture of acid chlorides was added slowly to 20 ml. (0.50 mole) of ice-cold absolute methanol. The solution was allowed to reach room temperature and then was refluxed for 1 hr. After washing the reaction mixture with saturated sodium bicarbonate solution, sodium thiosulfate solution and finally with water, the organic layer was taken up in ether, dried with magnesium sulfate, and distilled collecting the fraction boiling at 80–110°/100 mm. Fractionation yielded 4.72 g. (15%) of material of b.p. 100–102°/100 mm., n_D^{25} 1.4478.

Anal. Calcd. for $C_6H_9O_2Cl$: C, 48.49; H, 6.10; Cl, 26.54. Found: C, 48.49; H, 6.17; Cl, 26.44.

1-Chlorocyclobutanecarboxylic acid. Methyl 1-chlorocyclobutanecarboxylate (4.6 g., 0.031 mole) was dissolved in a mixture of 25 ml. of diethyl carbitol and 22.5 ml. of 12*N* hydrochloric acid (0.27 mole) and the mixture was heated at 98–105° for 16 hr. After cooling, the two-phase reaction mixture was extracted three times with a total of 100 ml. of

(18) L. Zechmeister and W. H. McNeely, *J. Am. Chem. Soc.*, **64**, 1919 (1942).

(19) All melting points are uncorrected. Microanalyses by A. Elek, Los Angeles, and Clark Microanalytical Laboratory, Urbana, Ill. Infrared spectra were determined using a Perkin-Elmer Model 21, Serial 122 or Model 137 Infracord spectrophotometer. The spectra were taken in carbon tetrachloride solution (0.050 g./ml.) using 0.05 mm. sodium chloride cells.

(20) J. Cason and C. F. Allen, *J. Org. Chem.*, **14**, 1036 (1949).

(21) H. Lemaire, with E. R. Buchman, unpublished results.

(22) J. R. Rischer, California Institute of Technology, M.S. thesis, with E. R. Buchman (1941).

TABLE III

DISTINGUISHING REGION (7.7–8.4 μ) IN THE INFRARED SPECTRA OF THE CYCLOBUTANECARBOXYLIC ACIDS

No-Cl	7.71	—	7.91	8.12	8.32
1-Cl	7.71	—	7.98	8.25	—
cis-2-Cl	—	7.85	8.02	8.15	—
trans-2-Cl	—	7.82	7.93	8.18	8.39
cis-3-Cl	—	7.77	7.96	8.12	—
trans-3-Cl	—	7.80	8.00	8.12	—

TABLE IV

MAJOR BANDS IN COMMON IN THE INFRARED SPECTRA OF THE HALO ACIDS AND THAT OF CYCLOBUTANECARBOXYLIC ACID (IN μ)

No Cl	1-Cl	*cis*-2-Cl	*trans*-2-Cl	*cis*-3-Cl	*trans*-3-Cl
3.38	3.41	3.40	3.39	3.40	3.38
5.84	5.83	5.81	5.84	5.83	5.83
7.00	7.04	6.92	7.00	7.00	6.98
10.62	10.85	10.80	10.65	10.65	10.65

ether. The combined ether extracts were shaken three times with a total of 30 ml. of 5% sodium hydroxide. The alkaline solution was neutralized and brought to a *p*H of 2–3 and extracted with a total of 50 ml. of ether. After drying over magnesium sulfate the ether solution was fractionated yielding 42% (1.76 g.) of material of b.p. 111–112°/12 mm., n_D^{25} 1.4545. The over-all yield from cyclobutanecarboxylic acid was *ca.* 5%. See Tables III and IV for infrared characterization data.

Anal. Calcd. for $C_5H_7O_2Cl$: C, 44.65; H, 5.25. Found: C, 44.58; H, 5.23.

2-Chlorocyclobutanecarboxylic acid mixture. A toluene solution of 1-cyclobutenecarboxylic acid[13] prepared from 39.9 g. of 1-bromocyclobutanecarboxylic acid[23] was dried over magnesium sulfate and then placed together with 0.5 g. of hydroquinone in a 300-ml. stirred autoclave. A tank of anhydrous hydrogen chloride was connected to the autoclave and the solution allowed to react for two hr. under continuous stirring at 600 p.s.i. The solution was removed and the toluene stripped under aspirator pressure. The product, 13 g., was collected 115–120°/6 mm. representing 43% yield based on the bromoacid.

Isolation of the 2-chlorocyclobutanecarboxylic acids. Mallinckrodt silicic acid (166.6 g.) specially prepared for chromatographic analysis by the method of Ramsey and Patterson[9] and 33.4 g. of Celite 545 (Johns-Manville) were placed in a mortar and thoroughly mixed. A solution was added of *exactly* 17 ml. of water, 80 ml. of absolute methanol, 15 drops of *freshly* prepared 1*N* ammonium hydroxide, and 10 ml. of Bromocresol Green indicator solution (0.200 g./25 ml. methanol) and the paste was mixed until a fine blue-green powder was obtained. Enough solvent-grade *n*-hexane was added so that the combined volume of the adsorbent and the hexane would just fill a 5.8 × 56 cm. glass tube which had a stopcock (2 mm. bore) sealed onto one end. A small cotton plug was placed in the bottom of the tube and, with the stopcock open, the mixture was added in one batch while the slurry was stirred vigorously. The column was tapped gently until the level of the silicic acid showed no settling over a period of 15 min.

A 2-g. sample of the acid mixture was taken up in 100 ml. of *n*-hexane and introduced onto the column in the usual manner. The column was developed with *n*-hexane, two bands clearly separating after 1100 ml. of eluate had passed through the column. Evaporation of the eluate from the fractions containing the first acid yielded a yellow oil which upon fractionation gave a colorless oil, b.p. 120–122.5°/14 mm., n_D^{23} 1.4713, the *trans*-2-chlorocyclobutanecarboxylic acid. See Tables III and IV for infrared characterization data.

Anal. Calcd. for $C_5H_7O_2Cl$: C, 44.65; H, 5.25. Found: C, 44.47; H: 5.16.

p-Bromophenacyl ester. Using 0.1 g. of the *trans*-2-chlorocyclobutanecarboxylic acid, the usual procedure[24] yielded crystals from water-ethanol, m.p. 73.6–74.1°.

Anal. Calcd. for $C_{13}H_{12}O_3BrCl$: C, 47.08; H, 3.65. Found: C, 47.15; H, 3.76.

Evaporation of the solvent from middle fractions of the second band yielded a solid which after recrystallization from petroleum ether melted at 97.0–98.5°, the *cis*-2-chlorocyclobutanecarboxylic acid. See Tables III and IV for infrared characterization data.

Anal. Calcd. for $C_5H_7O_2Cl$: C, 44.65; H, 5.25. Found: C, 44.47; H, 5.16.

p-Bromophenacyl ester. Using 0.1 g. of the *cis*-2-chloro acid the usual procedure[24] yielded crystals from water-ethanol, m.p. 88–89.5°.

Anal. Calcd. for $C_{13}H_{12}O_3BrCl$: C, 47.08; H, 3.65. Found: C, 46.57; H, 3.66.

2-Chlorocyclobutanecarboxylic acid chlorides. The *cis*-2-chloro acid (5.72 g., 0.0425 mole) was placed in a 3-necked 50-ml. flask equipped with a thermometer, condenser, and dropping funnel and protected with calcium chloride tubes. Phosphorus trichloride (2.5 ml., 0.0284 mole) was added, and the Glas-Col temperature raised slowly to 115° for 35 min. At this time 1.4 ml. of phosphorus trichloride was added and the solution allowed to reflux for 1 hr. The yellow solution was decanted and the remaining solid was washed with a little phosphorus trichloride. The solutions were combined and distilled from a 5-ml. distilling flask. The acid chloride (4.8 g.) was collected at 116–120°/68 mm. (74%). The *trans*-2-chloro acid chloride was prepared in 83% yield in the exact manner as described above. The fraction collected boiled between 104–106°/68 mm.

2-Chlorocyclobutanecarboxylic acid amides. The *cis*-2-chloroacid chloride (5.44 g., 0.0356 mole) was added to 20 ml. of ice cold concentrated ammonium hydroxide contained in a 50-ml. flask. The mixture was allowed to warm to room temperature. It was then boiled for a few minutes and allowed to cool. The cool solution was filtered and the precipitate was recrystallized from hot water, m.p. 160–165°.

Anal. Calcd. for C_5H_8ONCl: C, 44.94; H, 6.04. Found: C, 44.75; H, 5.83.

The *trans*-2-chloro acid amide was prepared in an identical manner, m.p. 144–145°.

Anal. Calcd. for C_5H_8ONCl: C, 44.94; H, 6.04. Found: C, 44.94; H, 5.68.

Methyl 2-chlorocyclobutanecarboxylates. Anhydrous methanol (3.5 ml.) was cooled to 0° and 4.8 g. (0.031 mole) of *cis*-2-chloro acid chloride was added dropwise over a 30-min. period. The mixture was allowed to warm to room temperature and then distilled collecting *cis*-ester at 110–115°/71 mm. giving 2.6 g. (56.6%), n_D^{25} 1.4517. The infrared spectrum of this compound showed absorption maxima ($CHCl_3$) at 2.84, 3.30, 5.68, 6.92, 7.32, 7.82, 7.98, 8.28, 8.49 μ.

Anal. Calcd. for $C_6H_9O_2Cl$: C, 48.50; H, 6.11. Found: C, 48.62; H, 6.10.

The *trans*-2-chloro ester was prepared as above yielding 33%, b.p. 103–105°/70 mm., n_D^{25} 1.4487. The infrared spectrum of this compound showed absorption maxima ($CHCl_3$) at 2.88, 3.34, 5.75, 6.98, 7.39, 7.88, 8.02, 8.30, 8.57 μ.

2-Chlorocyclobutyl cyanides. The *cis*-2-chloroamide (2.00 g., 0.015 mole) was mixed with 3.4 g. of phosphorus pentoxide and was distilled slowly from a 25 ml. pear-shaped distilling flask. The 0.53 g. yield (31%) boiled at 200–210°, n_D^{25} 1.4675.

(23) W. H. Perkins, Jr., and W. Sinclair, *J. Chem. Soc.*, **61**, 41 (1892).

(24) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., J. Wiley and Sons, Inc., New York, N. Y. (1959).

The infrared spectrum of this compound showed absorption maxima ($CHCl_3$) at 3.30, 4.40, 5.90, 6.90, 7.81, 11.35, 13.70, 14.40 μ.

Anal. Calcd. for C_5H_6NCl: C, 51.94; H, 5.20. Found: C, 52.07; H, 5.28.

The *trans*-2-chloro cyanide was prepared in the same manner 1.28 g. (0.0096 mole) of amide giving 0.88 g. (79%) of cyanide 125–130°/160 mm., n_D^{25} 1.4634. The infrared spectrum of this compound showed absorption maxima (chloroform) at 3.31, 4.40, 6.90, 7.81, 11.30, 13.70 μ.

Anal. Calcd. for C_5H_6NCl: C, 51.94; H, 5.20. Found: C, 52.17; H, 5.26.

1,1-Cyclobutanedicarboxylic acid dichloride. Thionyl chloride (342 g., 2.88 mole) was added dropwise to 104 g. (0.723 mole) of 1,1-cyclobutanedicarboxylic acid over a period of 20 min. The mixture was refluxed for 3 hr. after which time the yellow solution evolved little or no fumes. On fractionation 100 g. (77%) of material was obtained boiling at 108–110°/60 mm.

Diamide. The above dichloride (0.2 g.) was slowly added to 1 ml. of ice-cold ammonium hydroxide. The resulting precipitate was washed with cold water and recrystallized from hot water giving well defined prisms, m.p. 278–278.5° dec.

Anal. Calcd. for $C_6H_{10}O_2N_2$: C, 50.70; H, 7.04. Found: C, 50.65; H, 7.06.

3-Chloro-1,1-cyclobutanedicarboxylic acid dichloride. The 1,1-cyclobutanedicarboxylic acid dichloride (100.7 g., 0.556 mole), 2.33 g. of benzoyl peroxide, and 78.8 g. (0.584 mole) of sulfuryl chloride were refluxed until the temperature of the solution rose to 110° and few fumes were observed. (This required 1.5 to 2 hr.) The yellow to red-orange solution was fractionated yielding 62.8 g. (52%) of b.p. 96–98°/14 mm. material. The yield was raised to 60% by refractionating neighboring fractions. The starting material was recovered in 25% yield from lower boiling fractions.

Anal. Calcd. for $C_6H_5O_2Cl_3$: C, 33.41; H, 2.32. Found: C, 33.26; H, 2.39.

Diamide. The 3-chloro-1,1-cyclobutanedicarboxylic acid dichloride (0.2 g.) was converted to the diamide as outlined above. Recrystallization from hot water gave crystals, m.p. 212.5–213.8°.

3-Chloro-1,1-cyclobutanedicarboxylic acid. The 3-chloro-1,1-cyclobutanedicarboxylic acid dichloride (1.07 g., 0.005 mole) was treated with 1 ml. of water and with vigorous stirring the mixture was heated on a steam bath. After a brief induction period the reaction proceeded without external heating. Ether extraction of the resulting one-phase aqueous solution and subsequent evaporation yielded 0.89 g. (100%) of m.p. 135–142° dec. By repeated recrystallization from ethylene dichloride the decomposition point may be raised to 158–159.5°. Mixed m.p. with authentic material prepared by the method of Jones[11] showed no m.p. depression.

3-Chlorocyclobutanecarboxylic acid mixture. It is convenient to obtain these acids without isolation of the corresponding diacid. Accordingly, the crude mush from the ether evaporation occurring during the above diacid synthesis was directly heated to 180° for 20 min. and then fractionated collecting the portion distilling at 107–115°/4 mm. The yields averaged 66.2%.

Isolation of the 3-chlorocyclobutanecarboxylic acids. In a manner analogous to that for the isolation of the corresponding 2-chloro acids, a one-gram sample of the acid mixture was chromatographed. *n*-Hexane fractions containing the first acid were evaporated and recrystallized from petroleum ether at *ca.* −60° yielding a solid, m.p. 51–52.2° which showed no melting point depression with the 3-chlorocyclobutanecarboxylic acid obtained by Jones.[11] See Tables III and IV for infrared characterization data.

Anal. Calcd. for $C_5H_7O_2Cl$: C, 44.65; H, 5.25. Found: C, 44.69; H, 5.32.

p-Bromophenacyl ester. By the usual method[24] this acid gave needles, m.p. 110–111.2° from water-ethanol. The mixed melting point with pure *p*-bromophenacyl bromide (m.p. 109.8–110.5°) was 86–94°.

Anal. Calcd. for $C_{13}H_{12}O_3BrCl$: C, 47.08; H, 3.65. Found: C, 46.18; H, 3.84.

Effluent containing the second acid was evaporated and similarly purified at −60° from petroleum ether yielding a solid, m.p. 43.8–45.5°, the *cis*-3-chlorocyclobutanecarboxylic acid. A portion of this acid when mixed with a sample of the *trans*-3-chlorocyclobutanecarboxylic acid immediately melted at room temperature. See Tables III and IV for infrared characterization data.

Anal. Calcd. for $C_5H_7O_2Cl$: C, 44.65; H, 5.25. Found: C, 44.41; H, 5.57.

p-Bromophenacyl ester. This derivative[24] when recrystallized from water-ethanol gave a solid, m.p. 63.5–64.0°.

Anal. Calcd. for $C_{13}H_{12}O_3BrCl$: C, 47.08; H, 3.65. Found: C, 46.65; H, 3.82.

Methyl 3-chlorocyclobutanecarboxylates. A 1.9–2.5 g. sample of diazomethane in ether solution[25] was cooled in a dry ice–acetone bath and treated with less than the theoretical amount of *cis*-3-chloro acid and allowed to stand at room temperature for several hours. Fractionation yielded 86% of ester, b.p. 125–128°/100 mm., n_D^{25} 1.4538.

Anal. Calcd. for $C_6H_9O_2Cl$: C, 48.50; H, 6.11. Found: C, 48.83; H, 6.00.

The *trans*-3-chloro ester was prepared in the same manner in 57% yield, b.p. 118–125°/100 mm., n_D^{25} 1.4495.

Anal. Calcd. for $C_6H_9O_2Cl$: C, 48.50; H, 6.11. Found: C, 48.80; H, 6.12.

3-Chlorocyclobutanecarboxylic acid amides. The *cis*-3-chloro-ester (3.5 g., 0.024 mole) was taken up in 30 ml. of concentrated ammonium hydroxide and the mixture boiled until homogeneous. The solution was extracted with 3 × 30 ml. portions of ether and the extracts were evaporated. The amide (1.5 g., 48%) was repeatedly recrystallized from water and vacuum dried until constant melting at 172–173°.

Anal. Calcd. for C_5H_8ONCl: C, 44.94; H, 6.04. Found: C, 45.34; H, 5.97.

The *trans*-3-chloroamide was prepared in an identical manner in 53% yield, m.p. 188–190°.

Anal. Calcd. for C_5H_8ONCl: C, 44.94; H, 6.04. Found: C, 46.09; H, 6.27.

3-Chlorocyclobutyl cyanides. The *cis*-3-chloroamide (2 g., 0.015 mole) was mixed with 3.4 g. of phosphorus pentoxide and was distilled slowly, yielding 66% (1.15 g.) of *cis*-3 cyanide, b.p. 145–150°/120 mm., n_D^{25} 1.4699. The infrared spectrum of this compound showed absorption maxima ($CHCl_3$) at 3.21, 3.28, 4.38, 6.92, 7.74, 11.60, 14.50 μ.

Anal. Calcd. for C_5H_6NCl: C, 51.94; H, 5.20. Found: C, 51.90; H, 5.10.

The *trans*-3-chloro cyanide was prepared in the same manner in 92% yield, b.p. 120–125°/99 mm., n_D^{25} 1.4704. The infrared spectrum of this compound showed absorption maxima ($CHCl_3$) at 3.21, 3.28, 4.39, 6.97, 7.75, 12.10, 14.00 μ.

Anal. Calcd. for C_5H_6NCl: C, 51.94; H, 5.20. Found: C, 51.87; H, 4.83.

Infrared data. Spectral data suggest that each of the monochlorocyclobutanecarboxylic acids prepared above are chemical individuals (Table III) and that the cyclobutane ring is still intact (Table IV).

Isomerization data. One-tenth gram samples each of the 2-chloro acids and the 3-chloro acids were sealed in a separate 6 × 100 mm. glass tube containing 0.5 ml. of concentrated hydrochloric acid and placed for 30 min. in an oil bath preheated to 180°. The well blackened solutions were cooled, extracted with ether, and the ether solutions evaporated. The residues were separately boiled with benzene to remove water. The benzene residues were chromatographed on 20 g. (silicic acid–Celite) columns identical to the one described

(25) C. E. Redemann, F. O. Rice, R. Roberts, and H. P. Ward, *Org. Syntheses*, **Col. Vol. III**, 244 (1955).

TABLE V

DIPOLE MOMENTS OF CERTAIN CYCLOBUTANE COMPOUNDS

Compound	Dipole Moment ($\times 10^{18}$) at 25° in *p*-Dioxane
Cyclobutanecarboxylic acid	1.66 ± 0.09
cis-2-Chlorocyclobutanecarboxylic Acid	2.08 ± 0.05
trans-2-Chlorocyclobutanecarboxylic acid	2.44 ± 0.02
cis-3-Chlorocyclobutanecarboxylic acid	1.68 ± 0.11[a]
trans-3-Chlorocyclobutanecarboxylic acid	1.09 ± 0.02[a]
cis-1,2-Cyclobutanedicarboxylic acid[b]	2.71 ± 0.07
trans-1,2-Cyclobutanedicarboxylic acid[b]	1.84 ± 0.13
Methyl cyclobutanecarboxylate	1.96 ± 0.04
Methyl *cis*-2-chlorocyclobutanecarboxylate	2.40 ± 0.01
Methyl *trans*-2-chlorocyclobutanecarboxylate	1.51 ± 0.06
Methyl *cis*-3-chlorocyclobutanecarboxylate	2.86 ± 0.00
Methyl *trans*-3-chlorocyclobutanecarboxylate	2.61 ± 0.15
Cyclobutyl cyanide	3.48 ± 0.04
cis-2-Chlorocyclobutyl cyanide	4.41 ± 0.15
trans-2-Chlorocyclobutyl cyanide	3.52 ± 0.21
cis-3-Chlorocyclobutyl cyanide	2.92 ± 0.02
trans-3-Chlorocyclobutyl cyanide	2.15 ± 0.12

[a] *n*-Hexane solution. [b] E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, *J. Am. Chem. Soc.*, 64, 2696 (1942).

above. The results of titrating effluent fractions are shown in Table II.

Dipole moment data. The method employed was that of Guggenheim.[26] The dielectric constants were determined at 25° in purified[27] *p*-dioxane utilizing an E. H. Sargent (Chicago) Model V Chemical Oscillometer. Table V shows the dipole moments determined during the course of these experiments.

Chlorination of cyclobutanecarboxylic acid. Sulfuryl chloride (28.4 g., 0.210 mole) was slowly dropped into a solution of 20 g. (0.2 mole) of cyclobutanecarboxylic acid and 0.5 g. of benzoyl peroxide over a period of 15 min. The solution was brought to reflux in 15 min. and refluxed for 45 min. The mixture was fractionated and the portions boiling at 98–106°/14 mm. and 117–130°/9 mm. were combined and represented a 50% yield of monochlorocyclobutanecarboxylic acids.

Analysis of the chlorinated mixture was obtained by employing the chromatographic column previously described. Effluent fractions (10 ml. each) were titrated with 0.0197*N* sodium hydroxide. Titration results are shown in Table I. Identification of the peaks was made by the isolation of the respective acids and comparison with authentic materials by refractive index or mixed melting points.

Chlorination of cyclobutanecarboxylic acid chloride. The acid chloride (18.33 g., 0.15 mole) 13 ml. (0.16 mole) sulfuryl chloride and 0.5 g. of benzoyl peroxide reacted as described above for the acid. The reaction mixture was then treated with water at 100° for 1 hr. The aqueous solution was extracted with 3 × 25 ml. portions of ether. The combined ether extracts were dried over magnesium sulfate, evaporated, and the residue fractionated. The fraction b.p. 114–121°/11 mm. (5.40 g., 26%) was analyzed as described above and the results are given in Table I.

Chlorination of 1,1-cyclobutanecarboxylic acid. The dicarboxylic acid (28.8 g., 0.20 mole) and 0.5 g. benzoyl peroxide were slurried at 140 ml. benzene and 17.0 ml. (0.21 mole) of sulfuryl chloride was added dropwise at 130° over a period of 20 min. The mixture was then refluxed for 22 hr., the benzene removed by distillation and the residue decarboxylated at 180° for 30 min. The decarboxylated acid was fractionated and the fraction b.p. 113–125°/10 mm. (13.41 g., 50%) was analyzed as described above. The results are given in Table I.

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(26) E. A. Guggenheim, *Trans. Faraday Soc.*, 45, 714 (1949).

(27) L. F. Fieser, *Experiments in Organic Chemistry*, 3rd ed., revised, D. C. Heath and Co., Boston, 1957, p. 284.