TABLE IV

Expt	% d in III	% d in C_5 fragment	% IIIb of labeled III
4	83.3	35.9	43.2
6	90.0	38.8	43.2
8	92.2	38.7	42.0
9	85.0	35.6	41.9

The analogous calculation is carried out for the cyclopentadiene fragments[12,21] (m/e 66, 67).

$$\text{no. } d_0 = \text{intensity of } m/e \text{ 66} = 100$$

$$\text{no. } d_1 = 68.6 - (5.5\%)(100) = 63.1$$

where 5.5% of m/e 66 is the isotopic contribution[27] of m/e 66 to m/e 67. Thus

$$\%\ d_1 = \left(\frac{63.1}{100 + 63.1}\right)100 = 38.7\%$$

and

$$\%\ \text{IIIb} = \left(\frac{\%\ d_1 \text{ in cyclopentadiene ion fragment}}{\%\ d_1 \text{ in molecular ion}}\right)100 = \left(\frac{38.7}{92.2}\right)100 = 42\%\ \text{IIIb}$$

leaving 58% IIIa. Similar calculations for the experiments involving labeled III corresponding to Table I are given in Table IV. Mass spectral confirmation of labeled III results from observation that m/e 130 corresponds to 7.7% of m/e 129 due to labeled III plus 32% of the m/e 128 peak. The intensity of m/e 131 essentially corresponds to 32% of m/e 129 due to labeled III.

Stability of II under Reaction Conditions.—Samples of pure II (and I, where indicated) were added (in the amounts as indicated in Table V) to 50 ml of methylene chloride. The resulting solution was treated with hydrogen chloride gas under conditions listed for Table I above and for the times indicated in Table V. The samples were quenched with aqueous sodium carbonate and directly analyzed by pmr spectroscopy. The composition of the mixture was determined by integration of signals known to be due to each of I–IV. A sample of II subjected to these work-up conditions was stable and did not convert to I (by pmr).

TABLE V

II, ml	I, ml	Time of HCl addition, min	Time stirred, min	I, %	II, %	III, %	IV, %
0.50		10	60	4.7	0.6	76.3	18.4
0.50		10	60	0.0	1.8	81.8	16.4
0.50		5	20	1.7	5.2	77.6	15.5
0.25	0.25	5	20	0.0	8.0	78.8	13.1
0.25	0.25	5	20	1.8	5.0	81.0	12.2
0.50	0.50	5	0	2.8	1.2		

Registry No.—I, 121-46-0; II, 278-06-8; III, 3721-19-5; IIIa, 30715-36-7; IIIb, 30715-37-8; IV, 3509-46-4; HCl, 7647-01-0; DCl, 7698-05-7.

Acknowledgments.—Portions of this work were supported by the Research Corporation (grant to Terence C. Morrill) and by NSF-URP (department grant). We would like to thank Drs. E. Krakower and F. Elder of this department for the spectroscopic analyses, and R. E. Gilman for stimulating discussions.

Stereochemistry and Mechanisms of Cyclopropane Ring Cleavage. Addition of Hydrogen Chloride to Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylic Acid (Quadricyclenedicarboxylic Acid)

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Addition of hydrogen chloride to tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylic acid (**1**, quadricyclenedicarboxylic acid) under various conditions results in two products, *exo*-5-chlorotricyclo[2.2.1.0^{2,6}]heptane-2,*endo*-3-dicarboxylic acid (**4a**) and *exo*-5-chlorotricyclo[2.2.1.0^{2,6}]heptane-2,*exo*-3-dicarboxylic acid (**4b**). Thus with this cyclopropane ring, cleavage by nucleophile proceeds by inversion and (effective) addition of electrophile proceeds by a combination of retention and inversion. The results are interpreted in terms of a homoconjugate addition process.

Considerable attention has been centered on the stereochemistry of the addition of reagents (EX) to cyclopropanes which proceed by electrophile (E^+) transfer followed by nucleophile (X^-) attack.[2-8] It has been pointed out[2] upon scrutiny of these cases that the stereochemistry of electrophilic transfer can involve retention and/or inversion. Although paths rationalizing this this multiplicity can be understood (Figure 1),[2] the reason for choices among those paths has not been ex-

(1) Paper LXXI in the series Bridged Polycyclic Compounds. For the previous paper, see S. J. Cristol and R. Kellman, *J. Org. Chem.*, **36**, 1866 (1971).

(2) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, **92**, 4013 (1970).

(3) S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958).

(4) (a) A. Nickon and J. H. Hammons, *ibid.*, **86**, 3322 (1964); (b) J. M. Brown and M. C. McIvor, *Chem. Commun.*, 238 (1969).

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(7) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **90**, 4195 (1968); **92**, 571 (1970).

(8) (a) J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966); (b) A. Nickon, and N. H. Werstiuk, *ibid.*, **89**, 3914 (1967).

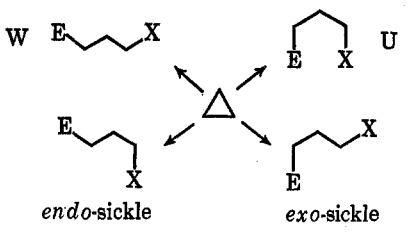
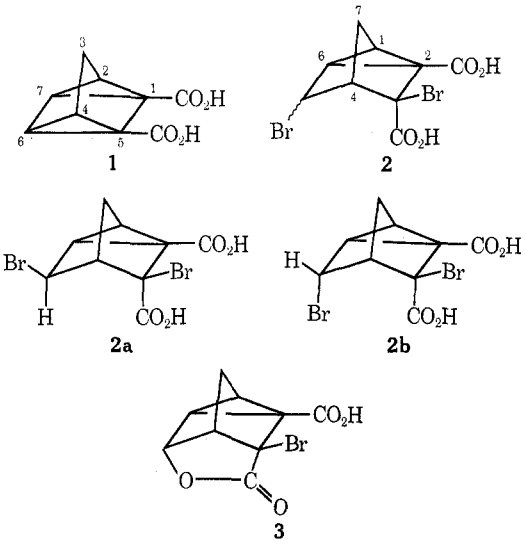


Figure 1.—Stereochemistry of cyclopropane ring cleavage (E^+ addition stereochemistry, X^- cleavage stereochemistry, respectively).[8b]

plained. It does appear that nucleophilic coordination always proceeds by inversion, except when carbonium ions intervene.[2]

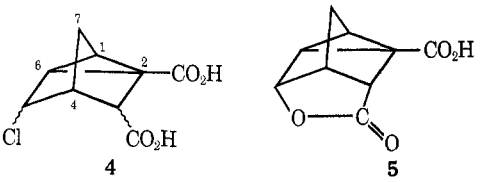
Closely related to the results we are now reporting is the observation[4] that treatment of nortricyclene with hydrogen chloride gives only *exo*-norbornyl chloride. Failure to form the endo isomer indicates that the nucleophilic attack proceeds entirely by inversion. The stereochemistry of the electrophilic cleavage of nortricyclene employing deuterium chloride is a mixture of retention and inversion.[4b] Similar experiments, using deuterioacetic acid, indicated a 1:1 ratio of inversion and retention cleavage processes involving the deuteron electrophile. Since no *endo*-norbornyl acetate was obtained, nucleophilic cleavage again occurred entirely by inversion.[4a]

Addition of bromine to tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane-1,5-dicarboxylic acid (**1**, quadricyclenedicarboxylic acid) has been reported[3] to give a dibromide(**2**), proposed to have either structure **2a** or **2b**. The carboxyl group was shown to be *endo* by the ready formation of lactone **3**. Structure **2a** appeared the more reasonable,



as it permitted the formation of **3** by a stereochemically allowed inversion process. **2b** seemed possible if one assumed that the bromine at C-5 is labilized by its being part of a cyclopropylcarbinyl system and if a carbonium ion intermediate preceded lactone formation. The latter possibility can be disregarded now, as much more has been learned about such systems.[9] At the time work was done on **2**, the product was assumed to contain only one isomer (**2a**). Whether this assumption would be borne out if modern analytical techniques were used is not known

Additions of hydrogen chloride to diacid **1** in aqueous and dioxane solvents have now been carried out. The hydrochlorides isolated from these addition reactions have the general tricyclic structure **4**, and samples pro-



duced under different solvent conditions vary only in the relative amounts of a pair of C-3 epimers. In the highly aqueous medium (0.33 *M* hydrochloric acid, University of Colorado), the reaction was complicated by the formation of alcohols (epimeric 5-hydroxytricyclo[2.2.1.$0^{2,6}$]heptane-2,3-dicarboxylic acids) and the γ-lactone of *endo*-5-hydroxytricyclo[2.2.1.$0^{2,6}$]heptane-2 *endo*-3-dicarboxylic acid (**5**).[3] In the early stages of the reaction, however, these side products comprise only a minor portion of the product. When dry dioxane saturated with hydrogen chloride gas was employed for the reaction, a side product, more volatile than **4** and believed to be an acid chloride of **1** and/or **4**, was formed in addition to adducts **4**. Use of dioxane solvent and enough concentrated hydrochloric acid to provide excess of hydrogen chloride resulted in quantitative conversion to the hydrochloride **4** in 5 min at room temperature. No side products were isolated (all dioxane solvent reactions were carried out at the Rochester Institute of Technology).

Hydrochloride adducts (**4**) were isolated from all of the above reactions in substantial yields. The conclusion that the samples differ only as to the composition of a pair of C-3 epimers of *exo*-5-chlorotricyclo [2.2.1.-$0^{2,6}$]heptane-2,3-dicarboxylic acids is based on the following information. Samples of **4** isolated from the aqueous reaction medium, mp 230–235 dec, were inert to dilute potassium permanganate and showed no olefinic absorption in the proton magnetic resonance (pmr) spectrum. Pmr absorption in the δ 4.0–4.5 region and at δ 2.70 each accounted for one proton. The signal at δ 2.70 (doublet, J = 1.5 Hz) was assigned to the proton at C-3 based on standard chemical shift data[10] for protons α to carboxyl groups and on related compounds.[11] The signals in the δ 4.0–4.5 region were resolved into a triplet at δ 4.34 (J = 0.9 Hz, 70% of one proton) and a broad singlet at δ 4.20 (30% of one proton); these are at appropriate chemical shifts for protons α to chlorine atoms.[10] The pmr spectrum of **4** at 100 MHz expands the frequency difference of these two signals from *ca.* 8 Hz (at 60 MHz) to 12 Hz. The rest of the nonexchangeable protons are in an envelope from δ 1.4–2.2. Mass spectral analysis of adduct **4** showed a molecular ion (M^+) at *m/e* 216 and an M + 2^+ ion intensity of 34.7% the intensity of M^+; this is consistent with the molecular formula $C_9H_9O_4Cl$ (especially one atom of Cl) for adduct **4**. The pmr spectrum (60 MHz) of the dioxane product was found to be identical with that for

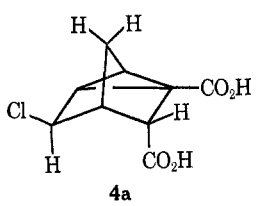
(9) S. J. Cristol, J. K. Harrington, and M. S. Singer, *J. Amer. Chem. Soc.*, **88**, 1529 (1966).

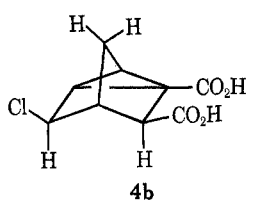
(10) R. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1963, p 137.

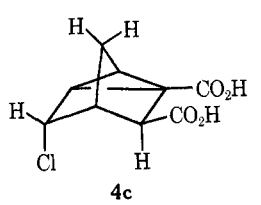
(11) (a) S. J. Cristol and J. K. Harrington, unpublished results; (b) J. K. Harrington, Ph.D. Thesis, University of Colorado, 1970.

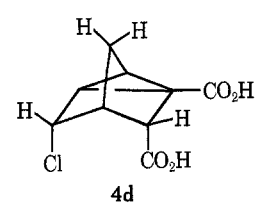
4 from the aqueous solvent reaction except that the signals at δ 4.34 and 4.20 integrated for 57 and 43% of one proton, respectively. The melting points for these samples were found to be 215–222° (from the nonaqueous dioxane reaction) and 208–213° (dioxane plus concentrated hydrochloric acid reaction). Thus it appears that all of these samples of hydrochloride 4 are epimeric mixtures of slightly differing composition, depending upon their origin. It seems likely that the Rochester results, in which the two isomers were formed in almost equal amounts, may be more reliable than the Colorado experiments, where fractionation preceding analysis may have occurred.

Samples of hydrochloride 4 from all of the above experiments were found to form lactone 5 when subjected to conditions previously reported.[3] The yield of 5 from the 4 mixture was not quantitative, but rather, in both cases studied, corresponded to that isomer whose C-5 proton absorbed at δ 4.34. Thus the 4 mixture resulting from the 0.33 *M* aqueous HCl experiment gave a 71% yield of 5. When the sample of 4 obtained from the dioxane-concentrated mineral acid mixture was subjected to lactone-forming conditions, the signal at δ 4.34 (57% of one proton) disappeared, the signal at δ 4.20 (43% of one proton in the original hydrochloride 4) remained, and a signal at δ 4.80 (consistent with the methine proton on the α carbon of an alcohol moiety of a lactone) appeared. The ratio, in the final lactone 5–unreacted 4 mixture, of the δ 4.20 and 4.80 signals was 46%/54%. These results confirm structure 4a as that of the major isomer of the adduct 4 and as the only precursor to lactone 5.


4a

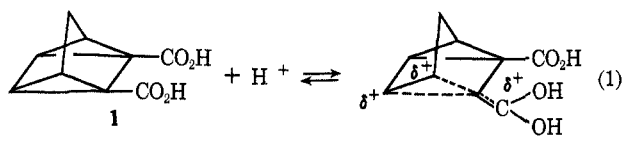

4b

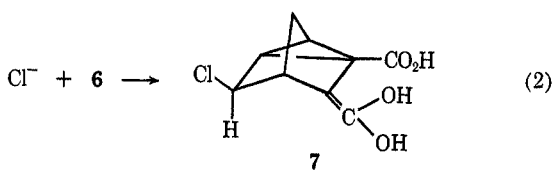

4c

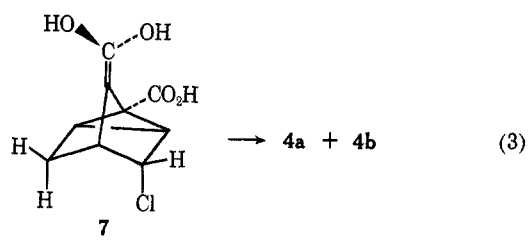

4d

Of the possible structures (4b, 4c, and 4d) for the other isomer, we have concluded that 4b is correct. Each of these would explain the lack of lactone formation, as none has appropriate stereochemistry. With 4a as a model, we note that (assuming C_{3v} symmetry) the C-3 proton (α to the carboxyl group) in 4b and that in 4d have essentially identical magnetic environments (1,3-diaxial proton–proton interactions), and should have identical chemical shifts (observed result, *vide supra*), while 4c should have a significantly deshielded proton.[12] This excludes 4c. Our experiments on hydration and addition of methanol[11] to 1 show that the two products formed in those reactions are analogous to 4a and 4b, and we therefore assign structure 4b to the minor isomer.

Additions of hydrohalic acids to cyclopropanecarboxylic acids were first observed by Kohler and Conant,[13] who noted that the rates of and directions of additions to these compounds were similar to those of α,β-unsaturated carbonyl compounds. The mechanism we are proposing for our results (eq 1–3) is in part based upon analogy to conjugate addition mechanisms[14] and in part to normal cyclopropane mechanisms.[2] Protonation of 1 is assumed to occur on one of the carboxyl groups to give the ion 6, which should have electron delocalization properties similar to that of a dihydroxycyclopropylcarbinyl cation. Attack by nucleophile at C-6 with inversion gives the *exo*-5-chloroenediol 7. Pre-


1 6 (1)


7 (2)


7 (3)

sumably attack at C-6 is favored over attack at C-4 in 6 because of the strain relief attendant upon opening of the cyclobutane (as well as the cyclopropane) ring.[15]

Compound 7, which is shown in different perspectives in eq 2 and 3, has almost identical steric environments for proton transfer to either side of the double bond involved in the enol–keto tautomerization to the carboxylic acid. It therefore seems understandable that both isomers (4a and 4b) are formed in the proton-transfer step. Thus the whole process is a homoconjugate addition, rather than a simple addition to the cyclopropane ring.

Ionic additions to quadricyclene (tetracyclo[3.2.0.-$0^{2,7}.0^{4,6}$]heptane) itself must utilize different processes from those of 1; substantial amounts of norbornenes are observed, as well as nortricyclenes.[17–20] These results require homoallylic rearrangement pathways and imply accompanying Wagner–Meerwein rearrangement;[21] neither of these sorts of rearrangements is observed in additions to 1. Presumably additions to quadricyclene involve transformations of protonated

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(13) E. P. Kohler and J. B. Conant, *ibid.*, **39**, 1404 (1917).

(14) E. S. Gould, "Mechanisms and Structure in Organic Chemistry," Holt–Dryden, New York, N. Y., 1959, pp 527 ff.

(15) Turner[16] has estimated the strain energy of quadricyclene relative to nortricyclene as 57 kcal/mol.

(16) R. B. Turner, P. Goebel, B. J. Mallon, W. v. E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

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(18) E. Vogelfanger, Ph.D. Thesis, University of California at Los Angeles, 1963.

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(20) T. C. Morrill and B. E. Greenwald, *J. Org. Chem.*, **36**, 2769 (1971).

(21) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2719 (1966).

cyclopropanes to carbonium ion intermediates. These are undoubtedly not involved with **1** because of the strong electron-attracting nature of the carboxylic acid substituents and the related availability of the carboxylic acid groups for protonation.

Experimental Section

Gas–liquid chromatography (glc) analyses were carried out on a Perkin–Elmer Model 154-D vapor fractometer: detector voltage, 8.0 V; recorder bridge, 1 mV. Columns were Pyrex glass and packed with 15% QF-1-0065 (Analabs) on 70–80 mesh Chromosorb W; the analytical column was 6 mm × 1 cm; the preparative column was 1 cm × 1 m. Response areas were integrated by planimeter and Disc integrator. Peak appearance is expressed as retention volumes. Infrared spectra were obtained on Beckman IR-5 and Perkin–Elmer 257 instruments. Proton magnetic resonance (pmr) spectra were obtained on Varian A-60, A-60A, and HA-100 and Perkin–Elmer R-20 (60 MHz) instruments. Chemical shifts are expressed as parts per million relative to TMS (δ = 0.00). Mass spectra were obtained from an Atlas Varian CH-5 instrument. Microanalyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn.; Huffman Microanalytical Laboratories, Wheatridge, Colo.; and Baron Consulting, Orange, Conn.

Preparation of Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylic Acid (1, Quadricyclenedicarboxylic Acid).—The preparation of **1** from norbornadienedicarboxylic acid has previously been described.[22] Scaling up of this reaction (30 g of diene–diacid) in 1500 ml of ether (GE AH-4 100-W lamp) and 58 g of diene–diacid in 4 l. of ether (Hanovia 450-W lamp, Pyrex sleeve) was also successful (yields 79 and 83%, respectively). Solubility, melting point, and infrared spectra were consistent with those reported earlier.[22] A pmr spectrum (sample from largest scale reaction) showed no olefinic absorption (δ 4.5–8.0).

Preparation of 5-Chlorotricyclo[2.2.1.0^{2,6}]heptane-2,3-dicarboxylic Acid (4) in Highly Aqueous Media.—Samples of **1**, weighing 16–22 mg, were sealed in small glass ampoules containing 1.0 ml of 0.33 *M* aqueous hydrochloric acid and allowed to stand for 24 hr at room temperature. The pH was adjusted to 4–5 by addition of aqueous potassium hydroxide. Water evaporation (room temperature) resulted in a residue which was extracted with hot reagent-grade acetone. Acetone was removed from the extracts (evaporation) and the residue was dissolved in *ca.* 0.3 ml of methanol. Dry ether containing diazomethane was added to the methanol solution until nitrogen evolution ceased and the yellow color persisted. Removal (evaporation) of ether and excess diazomethane resulted in a residue which was dissolved in reagent grade acetone and analyzed (glc) on the 1-cm QF column as containing 81% of the methyl ester of **4** (retention volume 2420 ml) and 19% of the methyl esters of 5-hydroxytricyclo-[2.2.1.0^{2,6}]heptane-2,3-dicarboxylic acid (retention volume 3700 ml).[11]

A preparative-scale synthesis of hydrochloride **4** was carried out as follows. A 560-mg sample of **1** and 24 ml of 0.33 *M* hydrochloric acid were combined in a flask; this mixture was heated (92°) with mixing for 6 min, at which time dissolution was complete. The mixture was cooled (ice) and brought to pH 3–4 with aqueous potassium hydroxide. Water removal (air stream) resulted in a residue; this residue was dried overnight in a vacuum desiccator ($CaCl_2$ drying agent, aspirator pressure), after which it weighed 710 mg. A small sample of this residue was treated with diazomethane (see preceding section), and glc analysis (QF column, 6 mm, 160°) showed three components, namely the methyl ester of **4** (64%, retention volume 790 ml), the esters of alcohol analogs (28%, retention volume 1200 ml), and the ester of lactone **5** (8%, retention volume 3090 ml).

A 162-mg sample of the residue was added to 1.0 ml of water. Initial dissolution was followed by precipitation. Filtration and drying yielded 56 mg of white crystals, mp 230–238° dec.

Anal. Calcd for $C_9H_9ClO_4$ (**4**): C, 49.90; H, 4.19. Found: C, 49.78; H, 4.10.

Pmr and mass spectral analyses of this precipitate were consistent with hydrochloride **4** (see text, 70% **4a**, 30% **4b**). Treatment of this precipitate with diazomethane (see above) and glc analysis (QF, 6 mm, 160°) gave 94% **4** esters and 6% alcohol ester.

Another 0.403 g of the original residue was added to 1.0 ml of water and 104 mg of **5** was collected. Ester formation and glc analysis (QF, 6 mm, 160°) gave 98.1% **4** ester (780 ml) and 1.9% ROH ester (1150 ml). A 104-mg sample of the adduct (**4**) was added to water and heated for 15–30 min on a steam bath. Product isolation, ester formation, and glc analysis (just as above) showed 85% **4** ester (780 ml) and 15% **5** ester (2970 ml) and no detectable ROH ester (1150 ml).

Conversion of 5-Chlorotricyclo[2.2.1.0^{2,6}]heptane-2,3-dicarboxylic Acid (4) to Lactone.—A mixture of 12.7 mg (0.059 mmol) of hydrochloride **4** (from the 0.33 *M* HCl preparation) and 0.5 ml of water was heated (92°) for 14.7 hr. Water was removed (rotary evaporator) and the resulting oil was dried. This oil was treated with diazomethane in ether (as above). Solvent was removed (evaporation) and the residue was analyzed by glc (6-mm QF column, 160°). Analysis indicated 29% unreacted hydrochloride ester (**4** ester, 750 ml) and 71% lactone ester (**5** ester, 3020 ml).

Preparation of Hydrochloride 4 in Dry Dioxane Solvent.—Into a stirred solution (room temperature) of 2.7 g (0.015 mol) of quadricyclenedicarboxylic acid (**1**) in 150 ml of dioxane was passed, *via* a fritted inlet tube, hydrogen chloride gas (Matheson Coleman and Bell). The gas was admitted (rapidly) for 1.5 hr to ensure saturation; during this time the solution volume increased by *ca.* 100 ml. Addition of gas was stopped and the mixture was allowed to stir overnight. The dioxane was removed (rotary evaporator) and from *ca.* 3 ml of solution a white solid precipitated. Filtering and drying (air) gave a white solid, mp 215–222°, yield 1.0 g (27%). Recrystallization was unsuccessful and proved unnecessary, as the precipitate analyzed correctly for hydrochloride **4**.

Anal. Calcd for $C_9H_9O_4Cl$: C, 49.90; H, 4.19; Cl, 16.37. Found: C, 49.68; H, 4.25; Cl, 16.28.

Pmr (in Polysol-d) indicated no olefinic protons (δ 4.5–8.0).

During removal of solvent a white solid was found in the trap to the rotary evaporator. This solid showed labile chlorine (to ethanolic silver nitrate) and was assumed to be an acid chloride of **1** and/or **4**. Further analysis proved unmeaningful.

A 200-mg sample of adduct **4** from this preparation was suspended in 40 ml of water and the mixture was heated at reflux for 1 hr. The solvent was removed (rotary evaporator) and the sample was air-dried. This sample showed a melting point of 180–190° and an infrared absorption (KBr) at 5.5–5.6 μ indicative of lactone **5**.[3]

Preparation of Hydrochloride 4 in Dioxane Using Concentrated Hydrochloric Acid.—A sample (10 g, 0.055 mol) of quadricyclenedicarboxylic acid (**1**) was dispersed in 150 ml of dioxane; addition of 33 ml (8 equiv) of concentrated hydrochloric acid resulted in virtually immediate dissolution (room temperature). After 5 min, one-tenth of the solution was quenched with water and worked up as described in the preceding section. Pmr analysis indicated 100% conversion of **1** to hydrochloride **4**, mp 209–211°. The remainder of the reaction mixture, after being stirred for 5 hr at room temperature, was quenched with water and worked up, as above. The total combined yield of adduct **4**, mp 208–213°, was 11.1 g (93%). Pmr analysis (Polysol-d) showed no olefinic absorption (δ 4.5–8.0) and was consistent with 57% **4a** and 43% **4b** (see text).

A sample (11 g) of **4** from the preceding preparation was placed in 2 l. of water and the mixture was heated at reflux for 2 hr. Solvent removal (rotary evaporator) resulted in solid, mp 189–191°. This sample gave a positive Beilstein test and a pmr spectrum (Polysol-d) consistent with 54% lactone **5** and 46% unreacted **4b**.

Registry No.—**1**, 30715-39-0; **4a**, 30715-40-3; **4b**, 30715-41-4; HCl, 7647-01-0.

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