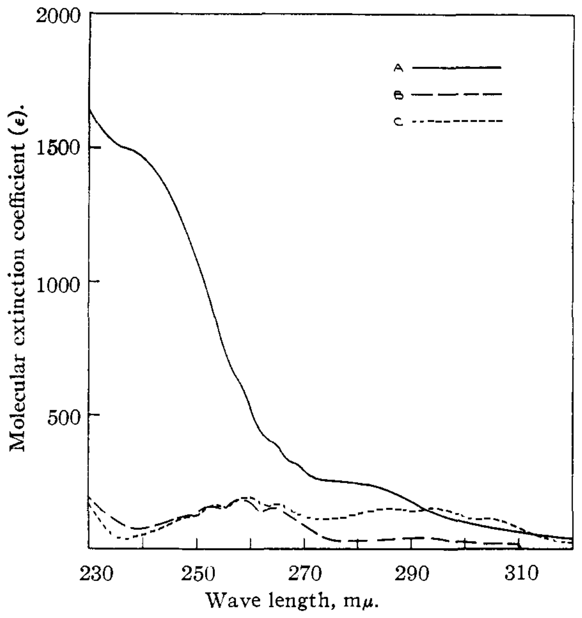

Fig. 1.—Ultraviolet spectra of: A, 2-phenylcyclopentanone; B, 2-phenylcyclohexanone (adapted from W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952)); C, 3-phenyl-2-butanone (adapted from W. D. Kumler, *et al.*[23]); solvent 95% ethanol.

violet and infrared spectra,[39] the ketone was freshly purified *via* the semicarbazone.[40] The ultraviolet spectrum (0.02 wt. % solution) is reproduced in Fig. 1; it is characterized by a shelf near 280 mμ, three shoulders in the 250–270 mμ region and a broad absorption band below 250 mμ. The infrared spectrum features a strong carbonyl band at 5.75 μ.

Resolution of 2-Phenylcyclopentanone.—The resolving agent was prepared[15] by conversion of methyl (+)-tartrate into methyl (+)-tartramide, m.p. 132–135°, $[\alpha]_D$ +57.8° (water) (lit.[15] m.p. 136–140°, $[\alpha]_D$ 62.9°), followed by conversion into the (+)-tartramazide, m.p. 147–148°, $[\alpha]^{25}_D$ +122° (water) (lit.[15] m.p. 146–148°, $[\alpha]_D$ 124°).

A solution of 43 g. (0.26 mole) of (+)-tartramazide and of 36 g. (0.225 mole) of 2-phenylcyclopentanone in 100 ml. of methanol was refluxed for three hours. The oil which separated on standing could not be induced to crystallize A solution of the oil in 3:1 methanol–chloroform, on standing in the refrigerator, deposited a crop of crystals. This material was recrystallized from the same solvent mixture ten times, until melting point and rotation had reached a constant value. There was thus obtained 0.75 g. of (+)-2-phenylcyclopentanone (+)-tartramazone, m.p. 151°, $[\alpha]^{27}_D$ +183.1° (*c* 4.98, methanol).

Anal. Calcd. for $C_{15}H_{19}O_4N_3$: N, 13.76. Found: N, 13.64.

The above tartramazone was added to a well-stirred refluxing mixture of ligroin and dilute hydrochloric acid. The ligroin layer yielded 0.2 g. of (+)-2-phenylcyclopentanone, m.p. 25–27°. Rotations[41] are recorded in Table IV.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.5; H, 7.55. Found: C, 82.4; H, 7.42.

Acknowledgment.—A grant-in-aid from Research Corporation is gratefully acknowledged.

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[39] In this connection, the assistance afforded by correspondence with Dr. Ralph Nusbaum and his staff, Spectroscopy Section, Atomic Energy Project, U.C.L.A., Los Angeles, Calif., is gratefully acknowledged.

[40] On prolonged standing, both 2-phenylcyclopentanone (W. Baker and P. G. Jones, *J. Chem. Soc.*, 787 (1951)) and 2-phenylcyclohexanone (W. E. Bachmann, G. I. Fujimoto and L. B. Wick, THIS JOURNAL, **72**, 1995 (1950)) are known to deteriorate.

[41] No claim for optical purity can be made, but it seems reasonable to suppose that the method employed in the hydrolysis of the tartramazone should be conducive to as negligible a degree of racemization as was observed in the hydrolysis of 2-phenyl-3-pentanone semicarbazone, under the same conditions.

NEW YORK 53, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Addition of Hydrogen Halides to α,β-Unsaturated Acids[1]

BY WYMAN R. VAUGHAN, ROBERT L. CRAVEN,[2] RANDEL Q. LITTLE, JR.,[3] AND A. CHARLES SCHOENTHALER

RECEIVED MAY 19, 1954

Evidence for the *trans* addition of hydrogen halides to α,β-unsaturated acids is reviewed and new evidence is presented to show that in general the addition occurs by a *trans* mechanism, which cannot involve formation of a simple enolic intermediate or a classical carbonium ion.

It has been assumed generally that hydrogen halides add to olefinic and acetylenic linkages in a *trans* sense. It is our purpose to establish the generality of this assumption as factual for olefinic acids in which the double bond is conjugated with the carboxyl group.

Fittig has reported that tiglic and angelic acids both afford the same hydrobromide,[4] but the hydroiodides of these acids differ, and upon dehalogenative decarboxylation, respectively, yield *trans*- and *cis*-butene[5] as would be expected from *trans* hydrohalogenation followed by *trans* dehalogenative decarboxylation.[6–9] In the same sense α-ethylcrotonic acid adds hydrogen iodide[10] and hydrogen bromide[11] to give hydrohalides both of which afford *trans*-2-pentene on treatment with base. Likewise *cis*-2-methyl-3-ethyl- and *trans*-2-methyl-3-ethylacrylic acids afford, respectively, *trans*- and *cis*-2-pentene by way of their hydroiodides.[12]

The formation of pure *meso*-2,3-dibromosuccinic acid by hydrobromination of bromomaleic acid would be convincing evidence for *trans* hydrobromination

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[1] Abstracted in the main from portions of the Ph.D. Dissertations of Robert L. Craven (1954) and Randel Q. Little, Jr. (1953), University of Michigan.

[2] American Brake Shoe Company Fellow 1951–1952, Albert B. Prescott Fellow in Organic Chemistry 1953.

[3] American Brake Shoe Company Fellow 1952–1953.

[4] R. Fittig and A. Pugenstrecker, *Ann.*, **195**, 108 (1879).

[5] W. G. Young, R. T. Dillon and H. J. Lucas, THIS JOURNAL, **51**, 2528 (1929).

[6] W. R. Vaughan and K. M. Milton, *ibid.*, **74**, 5623 (1952).

[7] S. J. Cristol and W. P. Norris, *ibid.*, **75**, 632, 2645 (1953).

[8] E. Grovenstein and D. E. Lee, *ibid.*, **75**, 2639 (1953).

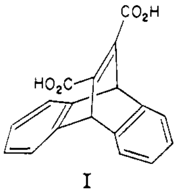
[9] R. L. Craven, Ph.D. Dissertation, University of Michigan, 1954.

[10] M. L. Sherrill and E. S. Matlack, THIS JOURNAL, **59**, 2134 (1937).

[11] W. M. Lauer and F. H. Stodola, *ibid.*, **56**, 1216 (1934).

[12] H. J. Lucas and A. N. Prater, *ibid.*, **59**, 1682 (1937).

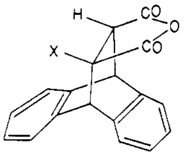
if the same paper did not report that bromofumaric acid also affords the same product, almost to the exclusion of the expected racemic form.[13] Clearly experimental evidence concerning the stereochemistry of the hydrohalogenation of α,β-unsaturated acids is suggestive of *trans* hydrohalogenation but is inadequate to permit any generalization; the single unequivocal case is the hydrobromination of dibenzo[2,2,2]bicyclooötatriene-2,3-dicarboxylic acid (I) in which only the product of *trans* addition is formed.[6]



I

The recent report that hydrogen bromide adds *trans* to simple monoölefins[14] is encouraging, but owing to the simpler system involved, it is not possible to transfer conclusions to the olefinic acid system without reservations.

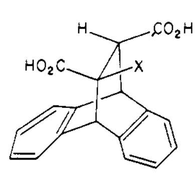
In connection with other studies in this Laboratory it seemed desirable to repeat the work of Vaughan and Milton[6] using hydrogen chloride. When the reaction was attempted in glacial acetic acid, saturated at 0° with hydrogen chloride, no reaction occurred after 12 hours, but at 135° for three days 2-chlorodibenzo[2,2,2]bicyclooöctadiene-*cis*-2,3-dicarboxylic anhydride(II) was obtained in 92.2% yield; apparently *cis* addition had occurred.



II, X = Cl IV, X = H

The investigations of Cristol and his collaborators on the dehydrochlorination of a closely related system[15] suggest that, since *cis* dehydrochlorination is encountered at elevated temperatures, the stereochemistry of hydrochlorination should be *cis*. The same work predicts that *trans* elimination should dominate at low temperatures, and consequently hydrochlorination should be *trans*, as for hydrobromination,[6] and in agreement we find that after eight days at 25° in 35% hydrogen chloride in glacial acetic acid a 67.7% yield of 2-chlorodibenzo[2,2,2]bicyclooöctadiene-*trans*-2,3-dicarboxylic acid (III) is obtained.

It is possible that addition at both temperatures is *trans*, and that II is formed by isomerization of III. The *trans*-acid III therefore was subjected to conditions under which I afforded II, and quantitative conversion occurred. Four processes may be considered for this isomerization: (A) Elimination of HX (only *trans* elimination is possible) followed by *cis* addition; (B) acid-catalyzed enolization, with essentially irreversible loss of water to give the anhydride II; (C) reverse Diels–Alder, followed by isomerization of chlorofumaric acid dehydration to the anhydride and readdition to anthracene; (D) bimolecular (S$_N$2) attack by chloride ion resulting in halide exchange–epimerization. This need not be considered for III because of the well-established hindrance to intermolecular nucleophilic displacement for this type of system.[6] For VII (below) this mechanism is less rigorously excluded even though potassium bromide is not very effective in epimerizing VII. Presumably this is attributable to the relatively low concentration of bromide from the potassium salt as compared with 30% hydrogen bromide.



III, X = Cl V, X = H

A number of reactions were run in an attempt to establish the nature of the isomerization, and the results are given in Table I. By way of ascertaining if elimination of hydrogen chloride was essential to the isomerization process, the deschloro analogs IV and V of II and III, respectively, were prepared from anthracene, maleic anhydride and fumaric acid.

Since reactions 4 and 5 (Table I) represent interrupted runs under identical conditions and for identical times, the similarity in yields suggests that the isomerization and dehydration of III to II (reaction 3) and the apparent *cis* hydrochlorination of I to II proceed through a common rate-controlling stage. The yield (60%) of II from anthracene and chloromaleic anhydride is significantly higher than in 4 and 5, and appreciable anthracene was recovered owing to the comparative slowness of the reaction. Thus since the Diels–Alder reaction is first order in both addends,[16,17] one would expect an appreciable build-up of anthracene in reactions 4 and 5 if process C were in-

TABLE I

HYDROCHLORINATION OF I AND EPIMERIZATION

Run	Reactant	Solvent[a]	Temp., °C.	Time, days	Product	Yield, %
1	I	a	135	3	II	92.2
2	I	b	25	8	III	67.7
3	III	a	135	3	II	98.0
4	III	a	135	6 hr.	II	36.1
5	I	a	135	6 hr.	II	36.4
6	III	c	135	3	I	52[b]
7	Fumaric acid and anthracene	a	135	3	IV	33.4
					V	32.8
8	V	a	135	3	IV	40.5
					V	52.2

[a] Solvents: a, hydrogen chloride–acetic acid, saturated at 0°; b, hydrogen chloride–acetic acid, 37%; c, glacial acetic acid. [b] Based on chloride ion.

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[13] M. S. Kharasch, J. V. Mansfield and F. R. Mayo, unpublished results; *cf.* J. V. Mansfield, Ph.D. Dissertation, University of Chicago, 1942.

[14] G. S. Hammond and T. D. Nevitt, THIS JOURNAL, **76**, 4121 (1954).

[15] S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952).

[16] A. Wasserman, *J. Chem. Soc.*, 828 (1935).

[17] W. E. Bachmann and L. B. Scott, THIS JOURNAL, **70**, 1458 (1948).

volved in the isomerization. Since no anthracene was detected, process C may be discounted. Support for either A or B, or a combination of the two, is adducible from reaction 8 which shows that an unfavorable equilibrium exists with respect to III; and this also may explain the failure to isolate III from any but the most highly concentrated hydrogen chloride solutions.

The failure to isolate anthracene from the isomerization of V (reaction 8), which actually afforded more IV than did reaction 7, again implies non-involvement of process C; and since reaction 8 cannot involve process A, it becomes evident that process B is of primary importance for isomerization. However, the fact that quantitative isomerization of III occurs (reaction 3) under conditions where less than 50% isomerization of V is observed (reaction 8) suggests that process A may be involved where it is possible. Alternatively one must invoke the generalization that a 2-substituted anhydride system is less readily opened (*i.e.*, is more stable) than the corresponding unsubstituted system in IV, thus admitting of a considerably less labile equilibrium in reaction 3. This generalization is justified by repeated observations in this Laboratory that 2- and 2,3-substituted derivatives of II or IV show increasing reluctance toward anhydride opening with increasing size of the substituents.[18] If this hypothesis is accepted, one may state that the isomerization proceeds principally by process B.

In order to determine this more definitely, a study was undertaken with cyclohexenecarboxylic acid (VI) whose hydrohalides might be interconvertible, but where the constitution of the equilibrium mixture would be governed by the thermodynamic stabilities of the *cis*-VII and *trans*-VIII forms without the complicating factor of subsequent anhydride formation. Both the 2-chloro and 2-bromo epimeric pairs were prepared, and, owing to the greater ease of preparation, the bromoacids were selected for study. The *trans* isomers were prepared from the appropriate *trans*-2-haloacrylic acids and butadiene, followed by hydrogenation; and each acid melted lower than its corresponding epimer, although the difference in melting points for the *cis*- and *trans*-bromoacids was only a few degrees. In order to obtain better evidence several attempts to equilibrate the bromoacids by heating each in the presence of bromide ion or hydrogen bromide were made. The results were not absolutely conclusive; however, comparatively little change was observed with the *trans* isomer while the *cis* isomer was altered extensively, as revealed by the melting points of the recovered acids.

Both the *cis*-chloro- and *cis*-bromoacid were prepared by hydrohalogenation of cyclohexenecarboxylic acid (VI). Since the principal product in each reaction was not identical with the *trans* isomers as prepared above, no doubt exists as to the configurations and, consequently, no doubt exists as to the stereochemistry of hydrohalogenation.

Analysis of a residue from one reaction, in which VI was shown to be absent, indicated that a certain amount of the *trans* isomer also was obtained during the hydrohalogenation reaction, but no entirely satisfactory method has been developed for estimating the exact relative quantities of *cis*- and *trans*-2-bromocyclohexanecarboxylic acids in such a mixture. An attempt to use infrared spectroscopy was abortive, since no clearly characteristic bands could be differentiated in synthetic mixtures. Accordingly, approximations based on a rough melting point–composition chart were used. In any case it appears that at moderate temperatures with a large excess of hydrogen bromide (in glacial acetic acid) some 62% of *pure cis* isomer is produced (*trans* hydrobromination), thus leaving *less* than 38% of the *trans* isomer in the recrystallization residues. Several crops of different melting point ranges were collected, and by comparison with the melting points of synthetic mixtures, it appears that there is not less than 40% and not more than 50% of the *trans* isomer in the residues. The composition of the residues is what might be expected from a crude melting point–composition diagram which indicates a eutectic of this approximate composition. Thus the extent of apparent *cis* addition is 15–18%. In a reaction run at 100–110° and using a smaller excess of hydrogen bromide there was obtained a 44% yield of pure *cis* isomer, and a 32% yield of mixed isomers was obtained as a second crop. If the latter is assumed to be about 50% *trans*, as suggested by its melting point range, this means that relatively more *trans* isomer is produced at the higher temperature.

It remains, then, to account for the formation of the *trans* isomer during hydrohalogenation (for the same situation appears to exist with hydrochlorination where only 66% of *cis* isomer is isolable). If one accepts the premise that the *trans* isomer is the more stable thermodynamically, as seems to be indicated by the extent of isomerization of the *cis* and *trans* forms under epimerizing conditions, the hypothesis that the composition of the mixture is thermodynamically controlled may be discounted. There must be considered, then, process A (which seems improbable since dehydrobromination of VII does not occur to any extent in refluxing acetic acid) and a modification of process B, omitting the subsequent anhydride formation. Since relatively less pure VII is recoverable after attempted epimerization under conditions approximating those for its formation from VI than is isolable from a preparative run, one may infer that such VIII as is formed in the preparative run results from epimerization and that the relatively lower quantity is a consequence of never having as high a concentration of VII during its actual preparation. Thus process B seems to be responsible for the product of apparent *cis* hydrobromination. Inferentially this conclusion may be applied to the bicyclic system as well, with the proviso that the more extensive isomerization of III as compared with V be attributed to the relative stabilities of the two anhydride systems

Finally it may be stated that hydrohalogenation of an olefinic bond conjugated with a carboxyl group proceeds by an essentially stereospecific mechanism in which the hydrogen and halogen be-

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[18] For a reported example see W. R. Vaughan and R. Q. Little, Jr., THIS JOURNAL, **76**, 4130, footnote 9 (1954).

come attached to opposite sides of the carbon–carbon π-bond. Control of the process is mechanistic rather than purely thermodynamic, but epimerization, at a slower rate, of the hydrohalide initially formed may occur to an extent governed by thermodynamic principles. The intermediate involved during such an epimerization is probably enolic, since no appreciable VIII is formed from VII and bromide ion; and since any rational representation of such a structure must admit of nearly equal probability of protonation from either side, it cannot be an intermediate in the hydrohalogenation process. By the same argument, initial protonation of the carbon–carbon π-bond to give a classical carbonium ion is excluded.

The evident strong dependence of hydrohalogenation on the concentration of hydrogen halide suggests a greater than first-order dependence on this reactant (*cf.* reference 14), and thus it is not profitable to speculate with regard to the exact nature of the mechanism without kinetic evidence, and there is no reason to suppose that such evidence as has been presented for non-polar solvents[19] can be transferred to reactions in glacial acetic acid. However, by ruling out an enolic intermediate during hydrohalogenation, it becomes conceivable that the mechanism may be the same for all olefinic bonds, whether or not[14] they are conjugated with a carboxyl group.

Experimental[20a,b]

Dibenzo[2,2,2]bicycloöctatriene-2,3-dicarboxylic Acid (I).—This compound was prepared according to the directions of Diels and Alder.[21]

2-Chlorodibenzo[2,2,2]bicycloöctadiene-*cis*-2,3-dicarboxylic Anhydride (II). A.—This substance was prepared according to the directions of Synerholm.[22] Under conditions identical to those for runs 4 and 5 (Table I) a 60% yield was obtained, whereas longer heating afforded a 90.9% yield.

B. By Addition of Hydrogen Chloride to I.—A solution of 2.00 g. (0.00684 mole) of I and 100 ml. of glacial acetic acid, saturated with hydrogen chloride at 0°, was heated in a sealed tube at 135° for three days. After allowing the excess hydrogen chloride to evaporate, the solution was treated with Norit and filtered. The partially crystallized oil obtained by evaporating the filtrate was triturated with a few ml. of toluene and dried in a vacuum desiccator; 2.09 g., m.p. 147.5–150.5° to a cloudy liquid. Fractional crystallization from toluene yielded 1.35 g. (63.5%) of II, m.p. 154.0–155.3°. No depression occurred in melting point when it was mixed with an authentic sample (155.0–156.5°) of II. In addition, there was obtained 20 mg. of impure I, 0.31 g. (14.5%) of less pure II and 0.13 g. of unidentified high melting solid.

C. By Isomerization of III.—A solution of 1.00 g. (0.00304 mole) of III and 50 ml. of glacial acetic acid, saturated with hydrogen chloride at 0°, was heated in a sealed tube at 135° for three days. After allowing the excess hydrogen chloride to evaporate, the solution was treated with Norit and filtered. The partially crystallized oil obtained by evaporating the filtrate was triturated with a few ml. of toluene and dried in a vacuum desiccator; yield 0.926 g. (98.0%), m.p. 149.5–153.0°. Recrystallization from toluene afforded pure II. II can be recovered in 86% yield from a mixture of I, II and III approximating the composition obtained in C.

2-Chlorodibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic Acid (III).—A mixture of 2.01 g. (0.00688 mole) of I, 30 ml. of glacial acetic acid and 19 g. of hydrogen chloride was sealed in a tube at the temperature of liquid air and allowed to stand at room temperature for eight days. After allowing the excess hydrogen chloride to evaporate, 0.08 g. of an insoluble inorganic material was separated. The filtrate was treated with Norit and evaporated to a partially crystallized oil, which completely solidified on drying overnight in a vacuum desiccator; yield 2.38 g., m.p. 192–198° dec. Crystallization from nitromethane gave 1.53 g. (67.6%) of III, m.p. 215–216° dec. Two recrystallizations from nitromethane raised the melting point to 217.5–218.5° dec.

Anal. Calcd. for $C_{18}H_{13}ClO_4$: C, 65.76; H, 3.98; Cl, 10.79. Found[23]: C, 65.79; H, 4.03; Cl, 10.54.

The methyl ester formed by the reaction of III with diazomethane was recrystallized from methanol two times; m.p. 141–142°.

Anal. Calcd. for $C_{20}H_{17}ClO_4$: C, 67.32; H, 4.80; Cl, 9.94. Found[23]: C, 67.39; H, 4.90; Cl, 9.75.

Comparative Rate of Formation of II from I and III. (A) By Incomplete Hydrochlorination of I.—A solution of 0.444 g. (0.00152 mole) of I and 25 ml. of glacial acetic acid, saturated with hydrogen chloride at 0°, was heated in a sealed tube at 135° for six hours. After allowing the excess hydrogen chloride to evaporate, the solution was treated with Norit and filtered. From the filtrate 0.147 g. (31.7%, corrected 36.4%) of II (m.p. 148.5–153.0°, mixed m.p. 150.5–154.5°) was isolated from the neutral fraction.

(B) By Incomplete Isomerization of III.—A solution of 0.500 g. (0.00152 mole) of III and 25 ml. of glacial acetic acid, saturated with hydrogen chloride at 0°, was heated in a sealed tube at 135° for six hours. After allowing the excess hydrogen chloride to evaporate, the solution was treated with Norit and filtered. From the filtrate 0.146 g. (30.9%, corrected 36.1%) of II (m.p. 150.0–153.5°, mixed m.p. 151–155°) was isolated.

Thermal Decomposition of III.—A solution of 0.501 g. (0.00152 mole) of III in 25 ml. of glacial acetic acid was heated in a sealed tube at 135° for three days. Nitrogen was passed through the reaction mixture and into a trap containing aqueous silver nitrate and 0.113 g. (0.000788 mole, 51.8%) of silver chloride separated.

After evaporating the reaction mixture to dryness, it was extracted with two 30-ml. portions of boiling water. From the cooled water extracts was obtained 0.171 g. of a white solid which softened to a semi-solid at 210° and melted at 230–236° dec. By refluxing 0.146 g. of this material with 1.5 ml. of absolute methyl alcohol and 0.1 ml. of concentrated sulfuric acid for seven hours, 0.117 g. of the dimethyl ester of I was obtained, m.p. 152.5–156.0°; mixed with an authentic sample (157.8–159.5°) it melted at 155.5–158.0° (previously reported[21] 160–161°).

***trans*-2-Chlorocyclohexene-4-carboxylic Acid.**—Four tubes were each charged with 5.8 g. (0.11 mole) of tank butadiene, 20–30 mg. of hydroquinone and 2.13 g. of *trans*-β-chloroacrylic acid[24] in 30 ml. of benzene. The tubes were sealed and heated for 30 hours at 150°. After opening the tubes, the slightly colored contents were removed and the solvent distilled off under reduced pressure. The rather gummy, slightly yellow solid residue weighed 14.61 g. This residue was dissolved only partly on treatment with 200 ml. of boiling petroleum ether (40–60°). The undissolved solid was filtered off, washed with petroleum ether and dried; 7.003 g., m.p. 108–110°, remained. Concentration of the filtrate by boiling yielded, on cooling to room temperature, 1.980 g., m.p. 108–110°; continued concentration gave 0.455 g. of gummy solid, m.p. 90–109°. A recrystallization of the latter material yielded 0.145 g., m.p. 108–110°. Attempts to recover more product by recrystallization from petroleum ether and from water or by sublimation of the very oily residue gave only small quantities of very impure solid. The latter was not included in the total yield which was 9.128 g., 71%. A second petroleum ether recrystallization narrowed and raised the melting point range to 108.6–109.8° cor. Further recrystallizations did not improve upon this value.

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[19] F. R. Mayo and J. J. Katz, THIS JOURNAL, **69**, 1339 (1947); F. R. Mayo and M. G. Savoy, *ibid.*, **69**, 1348 (1947).

[20] (a) Melting points are uncorrected unless otherwise noted. If corrected, the value is exact to ±0.5°. (b) Glacial acetic acid used was Baker and Adamson reagent; where 30% hydrogen bromide–acetic acid was used it was Eastman Kodak Co., White Label, 1161.

[21] O. Diels and K. Alder, *Ann.*, **486**, 191 (1931).

[22] M. E. Synerholm, THIS JOURNAL, **67**, 1229 (1945).

[23] Microanalysis by Clark Microanalytical Laboratory, Urbana, Ill.

[24] E. Gryszkiewicz-Trochimowski, W. Schmidt and D. Gryszkiewicz-Trochimowski, *Bull. soc. chim.*, 593 (1948).

Anal. Calcd. for $C_7H_9ClO_2$: C, 52.35; H, 5.65. Found[25]: C, 52.54; H, 5.69.

trans-**2-Bromocyclohexene-4-carboxylic Acid.**—Utilizing the same procedure as in the case of the chloro acid, 3.9 g. (0.072 mole) of butadiene and 2.023 g. (0.0134 mole) of *trans*-β-bromoacrylic acid[26] were sealed in a combustion tube with 50 ml. of benzene and a trace of hydroquinone. The tube was heated for 23 hours at 150°. After opening the tube, transferring the almost colorless homogeneous solution to a flask and removing the solvent in an air stream at room temperature, the white, slightly gummy crystalline residue was dried in a vacuum desiccator. The crude product, 2.952 g., was dissolved in boiling petroleum ether (60–75°) leaving behind only a trace of polymeric material. Filtration through a layer of Norit completely decolorized the light yellow solution. On cooling and standing at room temperature, clusters of colorless elongated prisms formed. This first crop after filtration, washing and drying weighed 0.877 g., m.p. 115–116°; a sample mixed with *trans*-β-bromoacrylic acid melted 80–107°. Subsequent crops brought the total yield of reasonably pure product, m.p. 114–116°, to 2.184 g. (79.5%). A second petroleum ether recrystallization of the material was effected with a 96% recovery in three crops, m.p. 115.0–115.6° cor. Further recrystallizations did not improve this value.

Anal. Calcd. for $C_7H_9BrO_2$: C, 40.99; H, 4.42. Found[25]: C, 41.28; H, 4.54.

trans-**2-Chlorocyclohexanecarboxylic Acid (VIIa).**—Hydrogenation of 23.18 g. (0.1443 mole) of *trans*-2-chlorocyclohexene-4-carboxylic acid in acetic acid over 0.2 g. of Adams catalyst gave, in four crops from petroleum ether (60–75°), 22.26 g. (94.4%) of white crystals, m.p. 85–86°. Repeated recrystallizations of the principal product raised the melting point to 84.0–85.7° cor.

Anal. Calcd. for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82. Found[25]: C, 51.93; H, 6.83.

trans-**2-Bromocyclohexanecarboxylic Acid (VIIb).**—Hydrogenation of 23.716 g. (0.115 mole) of *trans*-2-bromocyclohexene-4-carboxylic acid in 175 ml. of acetic acid over 0.2 g. of Adams catalyst afforded 23.62 g. of crude VIIb which was dissolved in boiling petroleum ether (60–75°) and was completely decolorized by filtration through a layer of Norit. Concentration and cooling of the filtrate afforded 20.32 g. of white crystalline solid, m.p. 108–109°. Subsequent crops brought the total yield of reasonably pure VIIb to 23.0 g. (96%). A second petroleum ether recrystallization raised the melting point to 109.0–109.8° cor. A sample mixed with the starting material melted at 98–106°.

Anal. Calcd. for $C_7H_{11}BrO_2$: C, 40.59; H, 5.35. Found[25]: C, 40.80; H, 5.46.

cis-**2-Chlorocyclohexanecarboxylic Acid (VIIIa).**—A combustion tube containing 4.26 g. (0.0338 mole) of cyclohexenecarboxylic acid[27,28] and 12 g. of glacial acetic acid was charged with anhydrous hydrogen chloride (8.0 g., 0.22 mole) and the tube was sealed and heated at 100–110° for 15 hours. Upon opening, the reaction mixture was decolorized completely by filtration through a 0.25-inch layer of Norit. The solvent and excess hydrogen chloride were removed as completely as possible using an aspirator and warming the reaction mixture at 70–80°. The almost white solid residue was stored over powdered potassium hydroxide in an evacuated desiccator for 12 hours; 5.33 g., m.p. 75–85°, with only a slight odor of acetic acid. This material was dissolved in about 40 ml. of boiling petroleum ether (60–75°) and processed as for VIIb, several crops being collected, m.p. 94–97°, 3.62 g. One recrystallization of the combined crops raised the melting point to 97.6–98.4° cor. with almost quantitative recovery; 3.60 g. (66.3%).

Anal. Calcd. for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82. Found[23]: C, 51.70; H, 6.87.

A sample of this compound mixed with an equal amount of the *trans* isomer melted at 60–90°.

cis-**2-Bromocyclohexanecarboxylic Acid (VIIIb).**—This compound was prepared using a modification of Aschan's procedure[29] from cyclohexenecarboxylic acid[27,28] and 30% hydrogen bromide in acetic acid. VIIIb was found to melt at 111.2–112.2°, reported[30] 112°.

Examination of the Low Melting Fractions.—A sample of the colored oily residue (m.p. 50–80°) obtained from the mother liquors from recrystallization of VIIIb was titrated with bromine for unsaturation. Assuming any olefin present to be unreacted starting material, the amount of the latter was not greater than 1.3%. The experimental error in determining pure cyclohexenecarboxylic acid by this method is 2–3%. Neutralization equivalent and alkaline hydrolysis to give bromide ion both corresponded to a product, $C_7H_{11}BrO_2$. After recrystallization from formic acid, a sample was submitted for microanalysis.

Anal. Calcd. for $C_7H_{11}BrO_2$: C, 40.59; H, 5.35; Br, 38.59. Found[23]: C, 40.85, 40.69; H, 5.47, 5.36; Br, 38.43, 38.40.

Isomerization Experiments. *cis*- **and** *trans*-**2-Bromocyclohexanecarboxylic Acids with 30% HBr-Acetic Acid.**—2.20 g. (0.0126 mole) of each isomer was sealed in separate tubes with 13.6 g. (0.0504 mole) of 30% HBr in acetic acid and maintained at a temperature of 100–110° for 24 hours. After cooling, the contents of the tubes (which had darkened somewhat) were washed into a flask with acetic acid and then partially neutralized with 0.05 mole of sodium bicarbonate. The precipitated solid was dissolved with water and then the water and acetic acid were removed by distillation at ~120 mm. The resulting oily solid was dissolved partially in 60 ml. of water and the remaining oil was taken up in 50 ml. of chloroform. The aqueous layer was washed with two 25-ml. portions of chloroform and the combined chloroform extracts were decolorized by passage through a 0.25-inch layer of Norit, dried, and concentrated. In the case of the *cis* isomer, 1.87 g. (85%) of material, m.p. 74.5–98.0°, was recovered (a crude phase diagram indicates at least 30% *trans* for this m.p.). The *trans* isomer yielded 1.82 g. (83%), m.p. 90–101° (no more than 10% *cis*, from a crude phase diagram). After five recrystallizations from 60–75° petroleum ether, the product from the *cis*-acid yielded 0.30 g. (16% of recovered material, 13.6% based on original sample) of nearly pure *trans*-acid, m.p. 107.0–108.5°, giving no depression with pure *trans*-acid, and m.p. 86–103° with authentic *cis* acid. Similarly, three recrystallizations of the *trans* product gave 0.58 g. (31.8% of recovered, 26.4% of original) of nearly pure *trans*-2-bromocyclohexanecarboxylic acid, m.p. 106–108°, 106.5–108.0° when mixed with pure *trans* isomer, 81–102° when mixed with pure *cis* isomer.

cis-**2-Bromocyclohexanecarboxylic Acid with Acetic Acid and Potassium Bromide.**—A mixture of 0.75 g. (0.00363 mole) of 2-bromocyclohexanecarboxylic acid and 0.432 g. (0.00363 mole) of potassium bromide was placed in 25 ml. of glacial acetic acid and allowed to reflux 24 hours. After cooling, most of the potassium bromide (not all of which had gone into solution) was filtered off and the acetic acid removed in an air stream. The resulting solid was triturated with 30 ml. of boiling petroleum ether and filtered. The solvent was removed in an air stream to give 0.49 g. (65.4%) of a white, waxy solid, m.p. 91–99° (indicating no more than 15% *trans;* mixed m.p. with pure *cis* 104.5–109°; mixed m.p. with pure *trans* 79–104°) after standing in a vacuum desiccator 48 hours.

cis-**2-Bromocyclohexanecarboxylic Acid with Acetic Acid.** The acid, 1.04 g. (0.0050 mole) of the acid (0.0050 mole) was refluxed 24 hours in 25 ml. of glacial acetic acid after which the solvent was removed in an air stream to yield 0.70 g. (67.3%) of waxy solid, m.p. 100.5–110.2° (90% *cis*) after three days in a vacuum desiccator.

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