Methyl 3-Cyclohexene-1-carboxylate (V).—Methylacrylate and butadiene were heated at 140° in a steel bomb for five hours, and the mixture distilled to afford 85% of methyl 3-cyclohexene-1-carboxylate (V).[20]

Methyl 1-Cyclohexene-1-carboxylate and Methyl 2-Cyclohexene-2-carboxylate.—The mixture of cyclohexenecarboxylic acids obtained from cyclohexanone cyanohydrin through cyclohexenecarbonitrile was fractionally crystallized from pentane to afford 1-cyclohexene-1-carboxylic acid which was esterified with diazomethane to afford methyl 1-cyclohexene-1-carboxylate, b.p. 105° (40 mm.), n^{25}_{D} 1.4808. The mother liquors from the fractional crystallization were fractionated, collecting the lower boiling fractions (enriched in 2-cyclohexene-1-carboxylic acid). Esterification with diazomethane was followed by fractionation to give the ester, methyl 2-cyclohexene-1-carboxylate, b.p. 94–95° (40 mm.), n^{25}_{D} 1.4605.

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[20] K. Alder and W. Vogt, *Ann.*, **564**, 120 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

Studies of Configuration. IV. The Rearrangement of Methoxycyclohexanecarboxylic Acids with Acetic Anhydride[1]

BY DONALD S. NOYCE AND HAROLD I. WEINGARTEN[2]

RECEIVED NOVEMBER 10, 1956

Treatment of *cis*-3-methoxycyclohexanecarboxylic acid with acetic anhydride and catalytic amounts of sulfuric acid leads to a mixture of three products, methyl cyclohex-3-ene-carboxylate, methyl *trans*-3-acetoxycyclohexanecarboxylate and methyl *trans*-4-acetoxycyclohexanecarboxylate. Under the same conditions *cis*-4-methoxycyclohexanecarboxylic acid leads to a mixture of the same products in different proportions. The mechanism of the rearrangement between the 3- and 4-positions is discussed. It is suggested that the rearrangement proceeds through a transition state which is doubly bridged.

In the previous paper of this series, it was shown[3] that the intramolecular rearrangement of γ- and δ-alkoxy carboxylic acid chlorides to the corresponding chloro esters could be extended to suitable derivatives of cyclohexanecarboxylic acid. Ethers may also be cleaved by acetic anhydride and acidic catalysts. Acetic anhydride has been reported to cleave ethers in the presence of catalytic amounts of Lewis acids such as boron trifluoride, zinc chloride, ferric chloride and aluminum chloride.[4] Nudenberg and Butz[5] reported the cleavage of 1,4-epoxycyclohexane with acetic anhydride and zinc chloride to *trans*-1,4-diacetoxycyclohexane. The cleavage of tetrahydrofurans has been investigated by Wilson[6] and Paul.[7]

In view of the apparent generality of the cleavage of ethers with acetic anhydride, it appeared feasible to demonstrate the intramolecular counterpart of this reaction. Such is the purpose of the present report.

The reaction between *cis*-3-methoxycyclohexanecarboxylic acid (*cis*-I), acetic anhydride and a small amount of sulfuric acid was investigated. Under these conditions, it would be expected that appreciable quantities of the mixed anhydride (II) of *cis*-I and acetic acid would be formed in equilibrium with acetic anhydride. The mixed anhydride (II) may then be expected to undergo intramolecular reaction to give methyl *trans*-3-acetoxycyclohexanecarboxylate (*trans*-III). The products were separated by fractional distillation. The lower boiling fraction was identified as methyl 3-cyclohexene-1-carboxylate (IV) as previously described,[3] and the higher boiling fraction (B) has the elemental composition and saponification equivalent appropriate for (*trans*-III).

It is to be noted that the isolation of esters III and IV clearly establishes the success of the *intramolecular* rearrangement. Were the methoxyl fragment ever to be released into solution, exclusive reaction with the solvent acetic anhydride would occur.

Further experiments designed to establish the structure of III showed that fraction B is in fact a mixture of isomers. Hydrolysis of fraction B afforded crystalline *trans*-4-hydroxycyclohexanecarboxylic acid (*trans*-V), identified by melting point and mixed melting point, and an oil. Crystallization of fraction B from pentane afforded the crystalline methyl *trans*-4-acetoxycyclohexanecarboxylate (*trans*-VI), identified by comparison with an authentic sample. Since it was apparent that fraction B was a mixture, several attempts were made to separate by crystallization some of the second component. These attempts failed. The composition of the mixture was determined by infrared analysis, by comparing the spectrum of fraction B with the infrared spectra of methyl *cis*-3-acetoxycyclohexanecarboxylate (*cis*-III), *trans*-III, methyl *cis*-4-acetoxycyclohexanecarboxylate (*cis*-VI) and *trans*-VI and with appropriate mixtures. The comparison of the infrared spectra indicated that only *trans*-III and *trans*-VI were present in the rearrangement product. Absorption bands at 12.22 and 10.15 μ characteristic of *trans*-III and at 7.60 μ, characteristic of *trans*-VI were observed. From the spectra of fraction B and of synthetic mixtures, it was determined that fraction B consisted of 57 ± 3% of *trans*-VI, and 43 ± 3% of *trans*-III.

cis-4-Methoxycyclohexanecarboxylic acid (*cis*-VII) was subjected to similar treatment with acetic anhydride and on fractional distillation two fractions were again obtained. The lower boiling fraction was IV, and the higher boiling fraction was

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[1] Presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955.

[2] Du Pont Summer Research Assistant, 1953; Eastman Kodak Fellow, 1954–1955.

[3] D. S. Noyce and H. I. Weingarten, THIS JOURNAL, **79**, 3093 (1957).

[4] H. Meerwein and H. Maier-Huser, *J. prakt. Chem.*, **134**, 51 (1932).

[5] W. Nudenberg and L. W. Butz, THIS JOURNAL, **66**, 307 (1944).

[6] C. Wilson, *J. Chem. Soc.*, 48 (1945).

[7] R. Paul, *Bull. soc. chim. France*, **53**, 417 (1933).

a mixture of ester acetates. The acetate fraction appeared at first to contain only *trans*-VI, but its infrared spectrum showed small inconsistencies in the regions where *trans*-III was known to absorb strongly. Therefore, the acetate fraction was crystallized from *n*-pentane yielding solid *trans*-VI and a filtrate. This filtrate was distilled and an infrared spectrum taken of the distillate. The analysis of this spectrum, made in the same way as before, revealed that the original acetate fraction contained approximately 5% of *trans*-III.

To show that the *cis* and *trans* isomers of the 3- and 4-methoxycyclohexanecarboxylic acids would behave differently, *trans*-I was subjected to the reaction conditions. Under these conditions *trans*-I yielded two products believed to be 3-cyclohexene-1-carboxylic acid and the anhydride of 3-cyclohexene-1-carboxylic acid.

Discussion

The first step in the intramolecular ether–acid anhydride rearrangement is clearly similar to that of the ether–acid chloride rearrangement,[2] the conversion of II (in the diaxial conformation) to the cyclic oxonium ion VIII. VIII may then proceed by any of three paths to products (Fig. 1). The first two, (a) elimination of a proton to yield methyl 3-cyclohexene-1-carboxylate (IV) and (b) solvolytic displacement by acetic acid to give methyl *trans*-3-acetoxycyclohexanecarboxylate (*trans*-III), completely parallel the analogous processes described previously.[3]

The third pathway (c), which produces methyl *trans*-4-acetoxycyclohexanecarboxylate (*trans*-VI) requires additional comment. The possibility that *trans*-VI arises by the addition of acetic acid to IV is ruled out by the fact that IV can be recovered in 80% yield from a reaction mixture of acetic anhydride, acetic acid and sulfuric acid after treatment under the conditions of the rearrangement. Further, the *cis*-3-methoxycyclohexanecarboxylic acid-*d* (prepared by equilibrating *cis*-I dissolved in toluene with D_2O) was treated with acetic anhydride with deuteriosulfuric acid as the catalyst. No deuterium could be detected in any of the products.

It is thus clear that an intramolecular hydrogen shift is responsible for the formation of *trans*-VI.

Intramolecular hydrogen shifts frequently have been suggested to proceed through a bridged cation transition state or intermediate.[8] Cram[9] has postulated ion-pair a as a possible intermediate in the rearrangement of 3-phenyl-2-butyl tosylates. Barnes[10] in proposing a mechanism for the formation of phenanthrene derivatives from β-arylethylcyclohexanols postulates ion b as an intermediate. To explain the formation of isobutyraldehyde in the solvolysis of 2-methoxy-2-methyl-1-propyl-*p*-bromobenzenesulfonate, Winstein, Lindegren and Ingraham[11] postulated ion c as a likely intermediate. Winstein and Holness[8a] also have postulated the bridged ions d and e to explain various products arising from the solvolysis of *cis*-4-*t*-butylcyclohexyl tosylate.

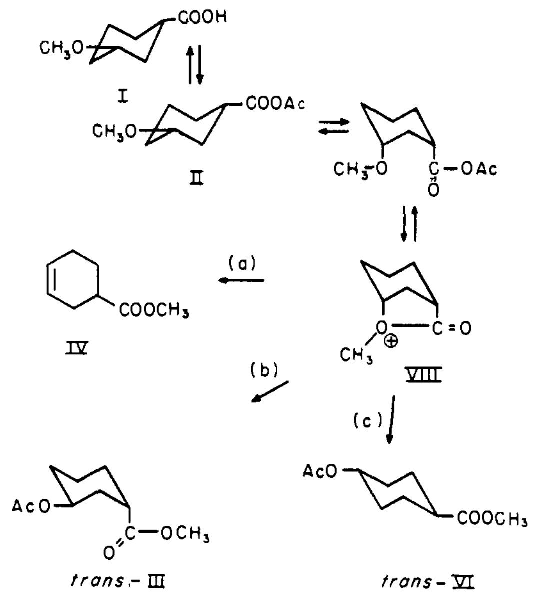
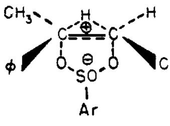
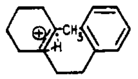


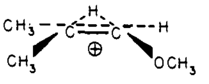
Fig. 1.



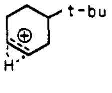
(a)



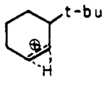
(b)



(c)

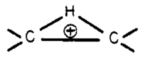


(d)

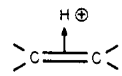


(e)

Cannell and Taft[12] suggest that the hydrogen bridge in a 1,2-shift is best represented by structure f in which the hydrogen is involved with the sp^3-hybrid orbitals of the carbon atoms rather than the π-complex (g) suggested by Dewar.[8b] This conclusion was reached after a study of migrations occurring upon the diazotization of isobutylamine in a deuterated solvent. Since exchange with the deuterated solvent was observed, Taft eliminates the π-complex (g) from consideration, which would rapidly exchange with the solvent,[13] and demonstrates the intramolecular nature of the reaction.



(f)



(g)

Mislow and Siegel[14] observed that in the rearrangement of optically active α-phenyl β-(*o*-tolyl)-

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[8] (a) S. Winstein and N. J. Holness, This Journal, **77**, 5572 (1955); (b) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford Univ. Press, Oxford, 1949, p. 144, etc.

[9] D. J. Cram, This Journal, **74**, 2137 (1952).

[10] R. A. Barnes, *ibid.*, **75**, 3004 (1953); R. A. Barnes and A. D. Olin, *ibid.*, **78**, 3830 (1956).

[11] S. Winstein, C. R. Lindegren and L. L. Ingraham, *ibid.*, **75**, 155 (1953).

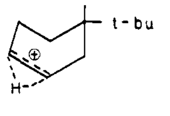
[12] L. G. Cannell and R. W. Taft, Jr., *ibid.*, **78**, 5812 (1956).

[13] R. W. Taft, Jr., Abstract of Papers, Joint Symposium on Mechanisms of Homogeneous and Heterogeneous Hydrocarbon Reactions, March, 1954, Kansas City, Missouri, p. 33.

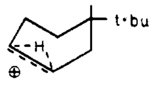
[14] K .Mislow and M. Siegel, This Journal, **74**, 1060 (1952).

ethylene glycol to phenyl-(*o*-tolyl)-acetaldehyde optical activity was retained. This fact suggests that the migrating hydrogen inverts the carbon to which it migrates and that the shift is simultaneous with the splitting off of the hydroxyl group. The inversion and simultaneity, furthermore, suggest as the reacting conformation one in which the hydrogen and hydroxyl are *trans* and coplanar. In the solvolysis of 2-alkylcyclohexyl tosylates, Winstein, *et al.*,[15] found the *cis* isomer a hundred times more reactive than the *trans*. These data also serve to point out the need for a *trans* coplanar conformation for neighboring hydrogen participation.

To explain the products formed by the addition of formic acid to 4-*t*-butylcyclohexene, Winstein and Holness[8a] suggest ions h and i as product giving intermediates. The assumption is made that the hydrogen-bridged ions tend to open stereospecifically to give axial products, by analogy with the direction of opening of steroidal epoxides[16] and with the addition of halogens to steroids.[17] The ion h yields *trans*-3 products while ion i yields *cis*-4 products.



(h)



(i)

The degree of migration and its stereospecificity will depend greatly on molecular structure and reaction medium.

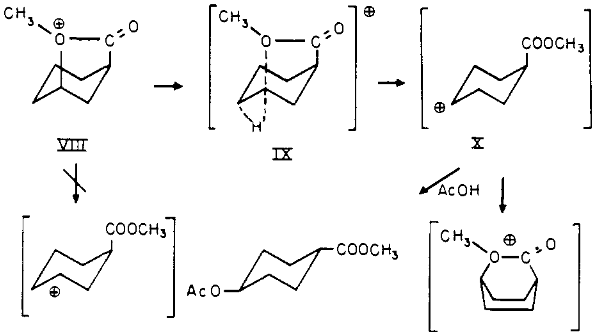


Fig. 2.

In the rearrangement under discussion, two mechanisms need consideration. In Fig. 2 the first mechanism is outlined. VIII, with hydrogen-4 axial and *trans* to the leaving oxonium oxygen, is ideally arranged for a hydrogen shift. As the carbon–oxygen bond is breaking the axial hydrogen-4 begins to migrate to the electron-deficient carbon-3 to yield the intermediate hydrogen bridged species IX. IX may open to give ion X which can react with acetic acid to form *trans*-VI, or it may internally coördinate to give oxonium ion XI, which can also react to give *trans*-VI. The possibility of ion VIII opening to the externally solvated ion XII prior to the migration of a hydrogen has been excluded for the following reason. If XII were formed, it would be expected to give largely *cis*-III; however, no *cis* products were ever observed. Likewise, *cis*-VI is the product expected to arise from the hydrogen bridged species, IX. Since no *cis* products are observed, the existence of IX is somewhat doubtful and it is preferable to exclude it as an intermediate. Further, were IX to open to the solvated "classical" carbonium ion X, the exclusive formation of *trans*-4 products would require internal participation by the ester grouping to give XI. The solvolytic studies of the 3-carbomethoxycyclohexyl tosylates reported[18] indicate that there is no transannular participation by the ester group. Such results make the transformation X → XI unlikely.

The mechanism for the rearrangement which is in accord with all the facts is presented in Fig. 3.

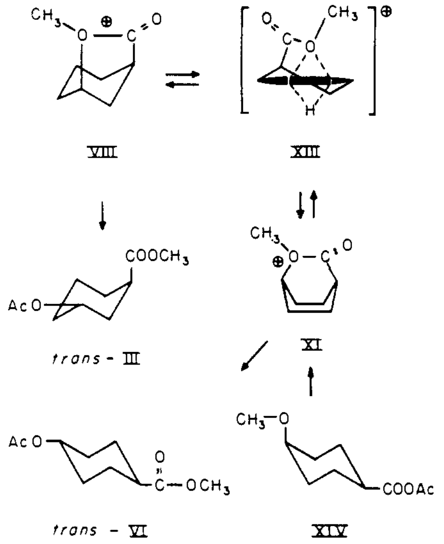


Fig. 3.

VIII is converted to XI in a single concerted process. As the bond of the oxonium salt to carbon-3 weakens, hydrogen bridging between carbons 3 and 4 occurs, and synchronous bridging of the oxygen to carbon-4 occurs. The doubly bridged ion XIII thus represents the transition state for that path leading to *trans*-VI from II. In like manner the small amount of *trans*-III resulting from the treatment of *cis*-VII with acetic anhydride and sulfuric acid may be considered to arise by the path VII → XIV, through XIII to VIII, to *trans*-III (Fig. 3). This pathway is then consistent with the formation of some *trans*-III to the exclusion of *cis*-III. Were the solvated carbonium ion XII formed by rearrangement from XI, the expected product would be largely *cis*-III.

An examination of the model of XIII reveals no unusual or prohibitive amounts of strain. An analogous doubly bridged species is suggested by Denney[19] as a transition state or short-lived intermediate for the rearrangement of the benzoate of

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[15] S. Winstein, *et al.*, THIS JOURNAL, **74**, 1127 (1952).

[16] L. F. Fieser, *Experientia*, **6**, 312 (1950).

[17] D. H. R. Barton, E. Miller and H. T. Young, *J. Chem. Soc.*, 2398 (1951).

[18] D. S. Noyce and H. I. Weingarten, THIS JOURNAL, **79**, 3103 (1957).

[19] D. B. Denney, *ibid.*, **77**, 1706 (1955).

9-decalyl hydroperoxide to 1-benzoyloxy-1,6-epoxycyclodecane.

There are several other reactions in which facile rearrangements in cyclohexane systems are observed. Examples are the Friedel–Crafts reactions of cyclohexene with *t*-butyl chloride,[20,21] with acetyl chloride and benzene,[22] of 1,2-dibromocyclohexane with benzene,[23] the conversion of 3-methylcyclohexanol to 1-chloro-4-methylcyclohexane (as a minor product) with hydrochloric acid,[24] and the conversion of 4-chlorocyclohexanol to a mixture of 1,3- and 1,4-dichlorocyclohexanes.[25]

It is attractive to suggest that many of these transformations also proceed through hydrogen bridged species, rather than by addition–elimination as has been suggested.[21]

Experimental[26]

Rearrangement of *cis*-3-Methoxycyclohexanecarboxylic Acid (*cis*-I) in Acetic Anhydride.—To a solution of 10 g. (0.063 mole) of *cis*-I in 50 ml. of acetic anhydride was added 0.2 g. of concentrated sulfuric acid. The solution was heated on a steam-bath for six hours, diluted with water and the aqueous mixture was extracted three times with *n*-pentane. The pentane extracts were combined and washed with sodium carbonate solution and water. After drying the extract over magnesium sulfate, evaporating and fractionally distilling the residue, two fractions were obtained. The first fraction, methyl cyclohex-3-enecarboxylate (IV), b.p. 94° (40 mm.), $n^{25}\mathrm{D}$ 1.4570, weighed 3.25 g. (37%). The second fraction (fraction B) was a mixture of methyl *trans*-3-acetoxycyclohexanecarboxylate (*trans*-III) and methyl *trans*-4-acetoxycyclohexanecarboxylate (*trans*-VI). The mixture was obtained to the extent of 38% (4.8 g.), b.p. 116–119° (7 mm.), and was characterized by infrared spectrum.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 60.1; H, 7.8.

Hydrolysis of Fraction B.—Two grams (0.01 mole) of fraction B was added to a solution of 3 g. (0.053 mole) of potassium hydroxide in 6 ml. of water and 3 ml. of methanol and the mixture placed on a steam-bath for one hour. At the end of this time the solution was poured into 100 ml. of water, washed once with pentane and acidified to a *p*H of 3. The oily material obtained after 12 hours of continuous extraction with ether was recrystallized three times from acetonitrile at 0° yielding 0.2 g. of *trans*-4-hydroxycyclohexanecarboxylic acid, m.p. 147.4–148.0° (lit.[29] m.p. 148°). A mixed melting point with authentic *trans*-4-hydroxycyclohexanecarboxylic acid showed no depression (m.m.p. 147–148°). The filtrates from the above recrystallizations yielded an uncrystallizable oil believed to be a mixture of *trans*-4-hydroxycyclohexanecarboxylic acid and *trans*-3-hydroxycyclohexanecarboxylic acid.

Isolation of Methyl *trans*-4-Acetoxycyclohexanecarboxylate (*trans*-VI).—Fraction B, 2.8 g., was crystallized from *n*-pentane in a Dry Ice-bath and was crystallized three times by decantation. The third precipitate was collected and recrystallized from *n*-pentane at 0° giving 0.7 g. (25%) of *trans*-VI, m.p. 48.0–48.5°. A mixed melting point with authentic *trans*-VI showed no depression.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 59.8; H, 8.1.

Separation of *cis*- and *trans*-3-Hydroxycyclohexanecarboxylic Acids.—Crystallization of the mixed acids (obtained by reduction of methyl *m*-hydroxybenzoate, followed by saponification) from ethyl acetate afforded *cis*-3-hydroxycyclohexanecarboxylic acid, m.p. 131.6–132° (lit.[27] 131.5°).

The phenacyl ester was prepared in the usual way[28] and was crystallized from benzene–pentane, m.p. 89.6–90.3°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.7; H, 6.9. Found: C, 68.8; H, 6.3.

The combined ethyl acetate filtrates from the above separation were evaporated and the residue heated on an oil-bath between 170 and 190° until the water which was formed no longer distilled over. The products were then separated by distillation. The first fraction, the lactone of *cis*-3-hydroxycyclohexanecarboxylic acid, b.p. 130–140° (20 mm.), weighed 7.0 g. (23%). The second fraction, 4.2 g. (12%) of *trans*-3-hydroxycyclohexanecarboxylic acid, b.p. 140–160° (5 mm.), was recrystallized four times from acetonitrile, affording 2.0 g. of *trans*-3-hydroxycyclohexanecarboxylic acid, m.p. 118.8–119.6° (lit.[27] 119–120°).

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.3; H, 8.4. Found: C, 58.8; H, 8.8.

A phenacyl ester was prepared in the usual way, and was recrystallized from benzene–pentane, m.p. 97.7–98.5°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.7; H, 6.9. Found: C, 68.6; H, 7.1.

Preparation of Methyl *trans*-3-Acetoxycyclohexanecarboxylate (*trans*-III).—*trans*-3-Hydroxycyclohexanecarboxylic acid, m.p. 118.8–119.6°, 1.5 g. (0.01 mole), was dissolved in ether and an excess of diazomethane in ether was added. After drying and removal of the ether the methyl *trans*-3-hydroxycyclohexanecarboxylate was fractionally distilled, b.p. 115–115.5° (5 mm.), to give 1.4 g. of the ester.

The methyl ester was then dissolved in 10 ml. of pyridine and 3 ml. of acetic anhydride. The resulting solution was heated on a steam-bath overnight, poured into water, acidified and extracted with pentane. The extract was dried over magnesium sulfate, evaporated and fractionally distilled, yielding 1.6 g. of *trans*-III, b.p. 122° (9 mm.), $n^{25}\mathrm{D}$ 1.4510.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 60.0; H, 8.1. Found: C, 60.0; H, 8.0.

Preparation of Methyl *cis*-3-Acetoxycyclohexanecarboxylate (*cis*-III).—*cis*-3-Hydroxycyclohexanecarboxylic acid, m.p. 131.6–132.0°, 2.4 g. (0.015 mole), was converted to *cis*-III as above. Three grams of *cis*-VIII was obtained, b.p. 112–113° (5 mm.), $n^{25}\mathrm{D}$ 1.4512.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 60.2; H, 8.3.

Separation of *cis*- and *trans*-4-Hydroxycyclohexanecarboxylic Acid Derivatives.—The crude mixture of *cis*- and *trans*-4-hydroxycyclohexanecarboxylic acid obtained by Raney nickel reduction of ethyl *m*-hydroxybenzoate, followed by alkaline hydrolysis, was dissolved in 100 ml. of pyridine and 100 ml. of acetic anhydride. The resulting solution was heated on a steam-bath overnight. Most of the pyridine and acetic anhydride were removed by distillation at reduced pressure and the residue was poured on to ice and acidified to a *p*H of 2. The resulting oil was extracted into ether, and the extracts were dried over magnesium sulfate, evaporated and the remaining oil distilled to yield two fractions. The first fraction, the lactone of *cis*-4-hydroxycyclohexanecarboxylic acid, 5.7 g. (21%), b.p. 120–140° (15 mm.), was recrystallized from benzene–pentane and 3.0 g. of lactone, m.p. 126–128° (lit.[29] m.p. 128°), was obtained. The second fraction, a mixture of *cis*- and *trans*-4-acetoxycyclohexanecarboxylic acids, b.p. 140–150° (3 mm.), weighed 18 g. (46%). Three recrystallizations from chloroform–pentane gave 6.2 g. of *trans*-4-acetoxycyclohexanecarboxylic acid, m.p. 137–139° (lit.[29] m.p. 139°). *cis*-4-Acetoxycyclohexanecarboxylic acid, 2.1 g., m.p. 81–83° (lit.[29] m.p. 80°), was obtained by repeated concentration and crystallization of the combined filtrates from which the *trans* isomer was largely removed.

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[20] J. H. Simons and A. C. Meunier, This Journal, **65**, 1269 (1943).

[21] L. Schmerling, *ibid.*, **69**, 1121 (1947).

[22] W. S. Johnson and R. D. Offenhauer, *ibid.*, **67**, 1045 (1945).

[23] C. D. Nenitzescu and D. Curcaneanu, *Ber.*, **70**, 346 (1937).

[24] L. H. Darling, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 1364 (1953); (b) D. S. Noyce and B. H. Walker, unpublished observations.

[25] E. L. Bennett and C. Niemann, This Journal, **74**, 5076 (1952).

[26] All melting points are corrected, boiling points are uncorrected. An 18" modified Podbielniak column was used for all fractional distillations. The infrared spectra were recorded by a Baird infrared spectrophotometer. Analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California.

[27] D. S. Noyce and D. B. Denney, This Journal, **74**, 5912 (1952).

[28] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd ed., 1948, p. 157.

[29] N. R. Campbell and J. H. Hunt, *J. Chem. Soc.*, 1379 (1950).

Preparation of Methyl *cis*-4-Acetoxycyclohexanecarboxylate (*cis*-VI).—Three grams (0.024 mole) of the lactone of *cis*-4-hydroxycyclohexanecarboxylic acid was heated with 10% potassium hydroxide for three hours. Following this period the solution was acidified to a *p*H of 2 and continuously extracted with ether. After drying the ether solution over magnesium sulfate, and evaporating to dryness, 2.4 g. (70%) of *cis*-4-hydroxycyclohexanecarboxylic acid was obtained. Crystallization from acetonitrile gave 2.0 g. of acid, m.p. 149.4–150.2° (lit.[29] m.p. 152°).

A phenacyl derivative was prepared in the usual way[28] and after one crystallization from benzene–pentane had m.p. 107.0–107.4°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.7; H, 6.9. Found: C, 68.6; H, 6.7.

The acid was dissolved in ether and an excess of diazomethane in ether was added. The solution was dried over magnesium sulfate, evaporated and the esterified product dissolved in 15 ml. of pyridine to which was added 7 ml. of acetic anhydride. The reaction mixture was heated on a steam-bath for six hours, poured into water, neutralized with dilute sulfuric acid and extracted twice with pentane. The pentane extracts were washed once with sodium carbonate solution, dried over magnesium sulfate, evaporated and the residual oil fractionally distilled. *cis*-VI, 2.3 g., b.p. 110° (5 mm.), $n^{25}\text{D}$ 1.4521, was obtained.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 60.2; H, 8.3.

Preparation of Methyl *trans*-4-Acetoxycyclohexanecarboxylate (*trans*-VI).—Two grams of 4-acetoxycyclohexanecarboxylic acid, m.p. 137–139°, was dissolved in ether and an excess of diazomethane in ether was added. The solution was dried over magnesium sulfate, the ether removed by distillation, and the residue was crystallized from *n*-pentane at −70°, yielding 1.4 g. of *trans*-VI. Two more crystallizations from *n*-pentane at 0° gave a product melting at 48.0–48.4°. The infrared spectrum was identical with that of the sample obtained from fraction B.

Behavior of Methyl 3-Cyclohexene-1-carboxylate (IV) under the Acetic Anhydride Rearrangement Conditions.—To 8.8 g. (0.063 mole) of IV was added 5.7 g. (0.095 mole) of acetic acid, 50 ml. of acetic anhydride and 0.2 g. of concentrated sulfuric acid. This solution was heated on a steam-bath for six hours and then poured into water and extracted into pentane. The pentane extracts were washed with water and sodium carbonate solution, dried, evaporated and the residue fractionally distilled. The recovered IV, 7.35 g. (83.5%), b.p. 94° (40 mm.), was the only product isolated.

Behavior of Methyl *trans*-3-Acetoxycyclohexanecarboxylate (*trans*-III) in the Acetic Anhydride Rearrangement Conditions.—To 4.25 g. (0.021 mole) of *trans*-III was added 30 ml. of acetic anhydride, 0.2 g. of concentrated sulfuric acid and 0.4 g. (0.022 mole) of water. This solution was treated in a manner identical with the foregoing experiment, and on fractional distillation of the crude product, 3.3 g. (77%) of *trans*-III was recovered. The infrared spectrum of the recovered ester was superimposable on that of authentic *trans*-III.

Behavior of *trans*-3-Methoxycyclohexanecarboxylic Acid (*trans*-I) in the Acetic Anhydride Rearrangement Conditions.—To 10 g. (0.063 mole) of *trans*-I was added 50 ml. of acetic anhydride and 0.2 g. of concentrated sulfuric acid and this solution was heated on a steam-bath for six hours. At the end of this time the solution was poured into water and extracted with pentane. The extracts were dried over magnesium sulfate, evaporated and the remaining oil fractionally distilled. The first fraction was 3-cyclohexene-1-carboxylic acid, b.p. 113–116° (5 mm.), m.p. 17–18.8° (lit.[30] m.p. 17°). The second fraction, believed to be the anhydride of the first, boiled at 128–132° (3 mm.) and had a saponification equivalent of 115 (calcd. 117).

Rearrangement of *cis*-4-Methoxycyclohexanecarboxylic Acid (*cis*-VII) in Acetic Anhydride.—*cis*-VII, 10 g. (0.063 mole), was treated in the same manner as *cis*-I and also yielded two fractions. The first, IV, weighed 3.2 g. (37%), b.p. 93° (40 mm.). The second was a mixture of *trans*-VI and *trans*-III, 4.7 g. (37%), b.p. 115° (5 mm.). This mixture was refractionated and an infrared spectrum obtained.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 60.3; H, 8.1.

Hydrolysis of the Mixed *trans*-VI and *trans*-III from the Rearrangement of *cis*-V.—Two grams (0.01 mole) of mixed *trans*-VI and *trans*-III was hydrolyzed under conditions identical to those employed for fraction B. Two crystallizations of the oily material obtained from the continuous extractions yielded 0.6 g. of *trans*-4-hydroxycyclohexanecarboxylic acid, m.p. 146.5–147.5° (lit.[29] m.p. 148°). A mixed melting point with authentic *trans*-4-hydroxycyclohexanecarboxylic acid showed no depression.

Isolation of Mixture of *trans*-III and *trans*-VI Enriched in *trans*-III from the Acetic Anhydride Rearrangement of *cis*-VII.—A sample of the mixed *trans*-III and *trans*-VI, 4.0 g., from the rearrangement of *cis*-VII, was recrystallized once from *n*-pentane at −70°. The supernatant solution was decanted and fractionally distilled to give a sample of the mixture enriched in *trans*-III, 0.8 g.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 59.9; H, 8.1.

Preparation of Sulfuric Acid-d_2.—From fuming sulfuric acid containing 30% sulfur trioxide was distilled 9.084 g. (0.1135 mole) of sulfur trioxide. This sulfur trioxide was then distilled into 2.26 g. (0.113 mole) of deuterium oxide through a simple distilling tube containing joints only for distilling flask, receiving flask and a vent leading to a calcium chloride drying tube. The distilling flask was heated in a water-bath while the very vigorous reaction of sulfur trioxide with heavy water was kept under control by keeping the receiving flask in cold water. A yield of 10.56 g. (93%) of product was obtained and shown by titration to be 97% deuteriosulfuric acid.

Preparation of *cis*-3-Methoxycyclohexanecarboxylic Acid-*d*.—To 20 g. (0.126 mole) of powdered *cis*-I in a dry separatory funnel was added 10.65 g. (0.53 mole) of deuterium oxide and the mixture was occasionally shaken over a 0.5-hour period. Dry toluene, 50 ml., was then added and the mixture shaken over another half-hour period. Then the two layers were separated and the toluene solution was placed in a distilling flask. The toluene and residual heavy water were distilled off at atmospheric pressure and the deuterated *cis*-I was distilled at 135–140° (3 mm.) yielding 18.9 g. (94%), m.p. 50.6–51.4°. Infrared analysis of deuterio *cis*-I showed the changes expected by deuteration.

Rearrangement of Deutero *cis*-I in Acetic Anhydride.—A solution of 9 g. (0.056 mole) of deuterio *cis*-I in 50 ml. of acetic anhydride, free of acetic acid, was prepared and 0.2 g. of 97% sulfuric acid-d_2 was added. The solution was kept on a steam-bath for 5.5 hours, then poured into 350 ml. of water and extracted with pentane. The extracts were washed with sodium carbonate solution, dried over magnesium sulfate, evaporated and the products fractionally distilled to give 3.2 g. (40%) of methyl 3-cyclohexene-1-carboxylate (IV), b.p. 92–93° (40 mm.). The infrared spectrum of IV was compared to the spectrum of an authentic sample and was shown to contain no deuterium. Also obtained was a mixture of *trans*-III and *trans*-VI, 4.5 g. (40%), b.p. 113–114° (5 mm.), from which pure *trans*-VI was isolated by crystallization from *n*-pentane, m.p. 48.0–48.5°. The infrared spectra of this *trans*-VI were compared with spectra of authentic samples at various concentrations and showed no deuterium content.

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[30] A. A. Petrov and N. P. Sopov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 2228 (1947); *C. A.*, **42**, 4957 (1948).