until once again the iodine coloration was gone. The mixture was cooled and filtered and the filtrate distilled. The 1,1-dichloro-3-iodo-1-propene had the following physical properties: b.p. 34° (1 mm.); $n^{20}\mathrm{D}$ 1.6030, $n^{25}\mathrm{D}$ 1.5998, $n^{30}\mathrm{D}$ 1.5968; $d^{20}{}_4$ 2.0480, $d^{25}{}_4$ 2.0401, $d^{30}{}_4$ 2.0300. *Anal.* Calcd. for $C_3H_3Cl_2I$: total halogen, 83.5; I, 53.6. Found: total halogen, 83.7, 83.7; I, 54.1, 54.0.

Lithium Aluminum Hydride Reduction of 1,1-Dichloro-3-iodo-1-propene from 3,3-Dichloro-2-propen-1-ol, Red P and I_2.—A mixture of 1,1-dichloro-3-iodo-1-propene (0.27 mole) and 10 ml. of ether was stirred rapidly while a suspension of lithium aluminum hydride (0.075 mole) in 20 ml. of ether was added at a rate to produce gentle refluxing. The excess lithium aluminum hydride was destroyed by 2% sulfuric acid and the organic layer was worked up in the usual manner. 1,1-Dichloro-1-propene (b.p. 75–76° (750 mm.); $n^{25}\mathrm{D}$ 1.4441) was obtained as the only product.

1,1-Dichloro-3-iodo-1-propene from 1,1,3-Trichloro-1-propene and KI.—1,1,3-Trichloro-1-propene (0.25 mole) was added slowly to 0.25 mole of potassium iodide in 600 ml. of acetone at 10°. The reaction product was worked up in the usual manner and gave 1,1-dichloro-3-iodo-1-propene as the only product. Its physical properties were: b.p. 34.5–35° (1 mm.); $n^{20}\mathrm{D}$ 1.6017, $n^{25}\mathrm{D}$ 1.5990, $n^{30}\mathrm{D}$ 1.5959; $d^{20}{}_4$ 2.0529, $d^{25}{}_4$ 2.0440, $d^{30}{}_4$ 2.0346. *Anal.* Calcd. for $C_3H_3Cl_2I$: total halogen, 83.5; I, 53.6. Found: total halogen, 83.8, 83.9; I, 54.0, 53.7.

Lithium Aluminum Hydride Reduction of 1,1-Dichloro-3-iodo-1-propene from 1,1,3-Trichloro-1-propene and KI.—The same procedure was used as in the reduction of the product obtained from the reaction of 3,3-dichloro-2-propen-1-ol, red phosphorus and iodine. The physical properties of the 1,1-dichloro-1-propene were: b.p. 75–76° (750 mm.); $n^{25}\mathrm{D}$ 1.4439.

1,1-Dibromo-3-chloro-1-propene.—A similar series of reactions were carried out for the preparation of 1,1-dibromo-3-chloro-1-propene from 1,1-dibromo-1-propene as used in the preparation of 1,1,3-trichloro-1-propene from 1,1-dichloro-1-propene. The yields and physical properties of the various compounds follow.

1,1-Dibromo-1-propene: b.p. 41.5° (30 mm.); $n^{25}\mathrm{D}$ 1.5245.

1,1,3-Tribromo-1-propene: yield 73%; b.p. 62–64° (0.5 mm.); $n^{20}\mathrm{D}$ 1.6030, $n^{25}\mathrm{D}$ 1.6006, $n^{30}\mathrm{D}$ 1.5980; $d^{20}{}_4$ 2.4408, $d^{25}{}_4$ 2.4304, $d^{30}{}_4$ 2.4207. *Anal.* Calcd. for $C_3H_3Br_3$: Br, 86.0. Found: Br, 85.7, 85.7.

3,3-Dibromo-2-propen-1-ol: yield 80%; b.p. 62–64° (0.5 mm.); $n^{20}\mathrm{D}$ 1.5652, $n^{25}\mathrm{D}$ 1.5633, $n^{30}\mathrm{D}$ 1.5611; $d^{20}{}_4$ 2.1788, $d^{25}{}_4$ 2.1707, $d^{30}{}_4$ 2.1632. *Anal.* Calcd. for $C_3H_4Br_2O$: Br, 74.0. Found: Br, 73.5, 73.6.

1,1-Dibromo-3-chloro-1-propene: yield 81%; b.p. 35.5–36.0° (0.6 mm.); $n^{20}\mathrm{D}$ 1.5663, $n^{25}\mathrm{D}$ 1.5634, $n^{30}\mathrm{D}$ 1.5610; $d^{20}{}_4$ 2.1365, $d^{25}{}_4$ 2.1260, $d^{30}{}_4$ 2.1162. *Anal.* Calcd. for $C_3H_3Br_2Cl$: total halogen, 83.3; Cl, 15.1. Found: total halogen, 83.4, 83.6; Cl, 14.7, 14.8.

1,1-Dibromo-3-iodo-1-propene from 3,3-Dibromo-2-propen-1-ol, Red P and I_2: b.p. 50° (0.1 mm.); $n^{20}\mathrm{D}$ 1.6737, $n^{25}\mathrm{D}$ 1.6708, $n^{30}\mathrm{D}$ 1.6681; $d^{20}{}_4$ 2.7283, $d^{25}{}_4$ 2.7171, $d^{30}{}_4$ 2.7060. *Anal.* Calcd. for $C_3H_3Br_2I$: total halogen, 88.0; I, 39.0. Found: total halogen, 88.3, 88.3; I, 39.1, 39.2.

Lithium Aluminum Hydride Reduction of 1,1-Dibromo-3-iodo-1-propene from 3,3-Dibromo-2-propen-1-ol, Red P, and I_2.—1,1-Dibromo-1-propene was the only product; b.p. 40° (29 mm.); $n^{25}\mathrm{D}$ 1.5245.

1,1-Dibromo-3-iodo-1-propene from 1,1-Dibromo-3-chloro-1-propene and KI: b.p. 51° (0.2 mm.); $n^{20}\mathrm{D}$ 1.6731, $n^{25}\mathrm{D}$ 1.6703, $n^{30}\mathrm{D}$ 1.6675; $d^{20}{}_4$ 2.7196, $d^{25}{}_4$ 2.7082, $d^{30}{}_4$ 2.6975. *Anal.* Calcd. for $C_3H_3Br_2I$: total halogen, 88.0; I, 39.0. Found: total halogen, 88.1, 88.2; I, 39.1, 39.3.

Lithium Aluminum Hydride Reduction of 1,1-Dibromo-3-iodo-1-propene from 1,1-Dibromo-3-chloro-1-propene and KI.—1,1-Dibromo-1-propene was the only product; b.p. 41° (30 mm.); $n^{25}\mathrm{D}$ 1.5247.

3,5-Dinitrobenzoates.—3,5-Dinitrobenzoates of the alcohols and all of the allylic halides were prepared using 3,5-dinitrobenzoyl chloride for the alcohols and the silver salt of 3,5-dinitrobenzoic acid for the halides. All of the alcohol derivatives with each of the corresponding allylic halide derivative showed no melting point depression. The melting point range for the dichloro derivatives was 69.5–70.8° and 90.2–91.2° for the dibromo derivatives. *Anal.* Calcd. for $C_{10}H_6Cl_2N_2O_6$ (from the alcohol): Cl, 22.1; N, 8.73. Found: Cl, 21.8, 22.0; N, 8.94. Calcd. for $C_{10}H_6Br_2N_2O_6$ (from the alcohol): Br, 39.0; N, 6.83. Found: Br, 38.6, 38.8; N, 7.05.

Reaction with Potassium Iodide in Acetone at 20°.—No consistent rate data could be obtained with either 1,1,3-trichloro-1-propene or 1,1-dibromo-3-chloro-1-propene. The weight of potassium chloride formed during the reaction indicated a 66% reaction in 15 minutes and an 88% reaction in 30 minutes.

Reaction of Sodium Ethoxide in Ethanol at 50°.—The procedure was the same as that previously described[4] and the data were calculated using the rate expression for a second-order reaction. The sodium ethoxide solution was 0.09931 molar for the reaction with 1,1,3-trichloro-1-propene (0.1025 molar) and 0.09182 molar for 1,1-dibromo-3-chloro-1-propene (0.1025 molar). A plot of log $b(a - x)/z(b - x)$ *vs.* time gave a straight line for 1,1,3-trichloro-1-propene between 26 and 81% reacted and for 1,1-dibromo-3-chloro-1-propene between 18 and 72% reaction. Selected data are given in Table I. Reaction of the vinyl halogens under these conditions was less than 1%.

AUSTIN, TEXAS

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

Studies of Configuration. III. The Rearrangement of Derivatives of 3- and 4-Methoxycyclohexanecarboxylic Acids[1]

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

RECEIVED NOVEMBER 10, 1956

The mechanism of the ether–acid halide rearrangement has been further clarified. The rearrangement of *cis*-3-methoxycyclohexanecarboxylic acid to methyl *trans*-3-chlorocyclohexanecarboxylate by the action of thionyl chloride has been studied. The *trans* isomer does not undergo rearrangement. These facts not only clarify the rearrangement process, but serve as independent evidence for the configuration of the isomers of 3-methoxycyclohexanecarboxylic acid. Similar results are obtained with 4-methoxycyclohexanecarboxylic acid. The cyclic oxonium ion intermediate opens by a process largely SN2 in character, with an additional factor of accelerated reaction in the case of ring-breaking displacement on a five-membered ring. Olefin formation accompanies the rearrangement. The olefin formed, methyl 3-cyclohexene-1-carboxylate is free of isomers, and this suggests that the elimination process is a synchronous reaction not proceeding from the simple carbonium ion.

The cleavage of ethers by acid halides has been investigated sporadically for many years. Benzoyl iodide was shown to cleave ether by Kishner.[3] Acid halides and acid anhydrides cleave ethers in the presence of Lewis acids.[4] These reactions un-

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(1) Presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955; previous paper, THIS JOURNAL, **75**, 127 (1953).

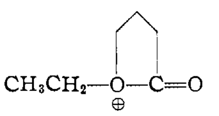
(2) Du Pont summer research assistant, 1953; Eastman Kodak Co. Fellow, 1954–1955.

(3) N. Kishner, *J. Russ. Phys.-Chem. Soc.*, **41**, 651 (1909); *Chem. Zentr.*, **80**, II, 1132 (1909).

(4) E. Wedekind and J. Haeusserman, *Ber.*, **34**, 2081 (1901); H. Meerwein and H. Maier-Hüser, *J. prakt. Chem.*, **134**, 51 (1932).

doubtedly involve the preliminary formation of an oxonium salt by reaction of the ether with the acid derivative, with concomitant weakening of the two carbon–oxygen ether bonds. The weakened carbon–oxygen bonds may then be subsequently cleaved bimolecularly or unimolecularly depending upon the structure of the molecule and the medium.

The intramolecular counterpart of these reactions also has received some attention. Blicke, Wright and Zienty[5] studied the rearrangement of γ-alkoxybutyryl chloride, but reached no conclusions concerning the mechanism. Prelog and Heinbach-Juhasz[6] investigated the kinetics of the rearrangement of ω-ethoxybutyryl chloride and ω-ethoxyvaleryl chloride to the ethyl ω-chloro esters, and found them to be first order in the acid chloride. The reaction was pictured as proceeding through the cyclic oxonium ion I which could react with chloride ion to form the ester. Wiberg[7] showed that with an optically active homolog, the second step in this sequence was stereospecific with inversion.



I

In the present study, we have shown that the further consequence of this mechanism, namely, that a suitably chosen pair of *cis* and *trans* isomers should show distinctive differences in behavior, is correct.

Pure *cis*-3-methoxycyclohexanecarboxylic acid (*cis*-II) was obtained by fractional crystallization from pentane of the mixed *cis*- and *trans*-II obtained by reduction of *m*-methoxybenzoic acid. When *cis*-II was heated with phosphorus tribromide at 100° for two hours, there resulted 80% of methyl *trans*-3-bromocyclohexanecarboxylate (III) and a small quantity of an unsaturated ester. The structure of III was established by unambiguous synthesis. The lactone of *cis*-3-hydroxycyclohexanecarboxylic acid was converted to *trans*-3-bromocyclohexanecarboxylic acid of melting point 65°[8] with hydrogen bromide and esterified with diazomethane to give III. Though Perkin and Tattersall[9] originally assigned the *cis* configuration to the 65° isomer, Siegel and Morse have pointed out that it is undoubtedly *trans*. III could not be hydrolyzed successfully to the known acid of m.p. 65° due to its instability in hydroxylic solvents. This instability also has been observed by Siegel and Morse, and constitutes additional evidence for the *trans* configuration of the 65° isomer. Comparison of the infrared spectra of the synthetically prepared III and III resulting from the rearrangement revealed no differences.

When *cis*-II was heated in thionyl chloride for two hours, two products subsequently were isolated, the expected methyl *trans*-3-chlorocyclohexanecarboxylate (IV) and methyl 3-cyclohexene-1-carboxylate (V). IV and V, formed in the ratio of 3:5, were isolated in a combined yield approaching 90%. Acidic hydrolysis of IV gave *trans*-3-chlorocyclohexanecarboxylic acid, m.p. 52°. The structure was assigned on the basis of the analogous bromine compounds.

The olefinic ester V from the rearrangement, isolated in minor quantities in the treatment of *cis*-II with phosphorus tribromide, and in major quantities on treatment of *cis*-II with thionyl chloride, was shown to be methyl 3-cyclohexene-1-carboxylate by comparison of the infrared spectrum with that of an authentic sample prepared from methyl acrylate and butadiene. The infrared spectra of the two alternate isomers showed distinctive differences. There was no evidence for the presence of any of the isomers within the limits of accuracy of the analysis.

To determine the generality of the ether acid halide rearrangement in the cyclohexanecarboxylic acid derivatives, pure *cis*-4-methoxycyclohexanecarboxylic acid (*cis*-VI) was prepared and treated with both thionyl chloride and phosphorus tribromide. *cis*-VI was prepared by high pressure hydrogenation of methyl anisate, the derived methyl 4-methoxycyclohexanecarboxylate being then hydrolyzed and the 4-methoxycyclohexanecarboxylic acid separated into its component isomers by fractional crystallization.

On heating in thionyl chloride *cis*-VI gave rise to methyl *trans*-4-chlorocyclohexanecarboxylate (VII) and V in a ratio of 3:4 and in an over-all yield of 80%. Rearrangement of *cis*-VI in phosphorus tribromide led to the formation of 58% of methyl *trans*-4-bromocyclohexanecarboxylate (VIII) and 16% of *trans*-4-bromocyclohexanecarboxylic acid, which could have arisen either by cleavage of VIII or *cis*-VI.

VIII was hydrolyzed in low yield to the *trans*-4-bromocyclohexanecarboxylic acid, m.p. 170.8–171.4°, which compares favorably with the value, 167°, recorded by Perkin.[10] *trans*-4-Chlorocyclohexanecarboxylic acid, m.p. 159.0–159.8°, obtained by hydrolysis of VII in 88% yield, has to our knowledge not been reported previously in the literature. The structure is assigned by analogy with the acid obtained from VIII.

When the *trans*-3-methoxycyclohexanecarboxylic acid (*trans*-II) was subjected to treatment with thionyl chloride, the acid chloride was obtained. In fact, treatment of the mixed isomers of II obtained directly from the hydrogenation with thionyl chloride followed by treatment with water, led directly to the isolation of *trans*-II, with *cis*-II being converted to IV and V. In like fashion, *trans*-4-methoxycyclohexanecarboxylic acid (*trans*-VI) with thionyl chloride was converted to the acid chloride and did not undergo rearrangement. The treatment of *trans*-II and *trans*-VI led to reaction different from that observed with the *cis* isomers.

Discussion

The following sequence is in accord with the facts presented here and the discussion which fol-

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[5] F. F. Blicke, W. B. Wright, Jr., and M. F. Zienty, THIS JOURNAL, **63**, 2488 (1941).

[6] V. Prelog and S. Heinbach-Juhasz, *Ber.*, **74**, 1702 (1941).

[7] K. B. Wiberg, THIS JOURNAL, **74**, 3957 (1952).

[8] S. Siegel and J. G. Morse, *ibid.*, **75**, 3857 (1953).

[9] W. H. Perkin and G. Tattersall, *J. Chem. Soc.*, **91**, 482 (1907).

[10] W. H. Perkin, *ibid.*, **85**, 431 (1904).

lows. The first step is the formation of the acid halide (IX), which in the diaxial conformation IXa may undergo intramolecular displacement of the halide ion to give the bicyclic oxonium salt X. There are several pathways of reaction open to X, and each presents points of interest. X may undergo (a) elimination of a proton to give the unsaturated ester which has been shown to be V; (b) reaction with halide ion at carbon-3 to give III or IV; (c) reaction with halide ion at the methyl carbon to give the lactone or products resulting therefrom.

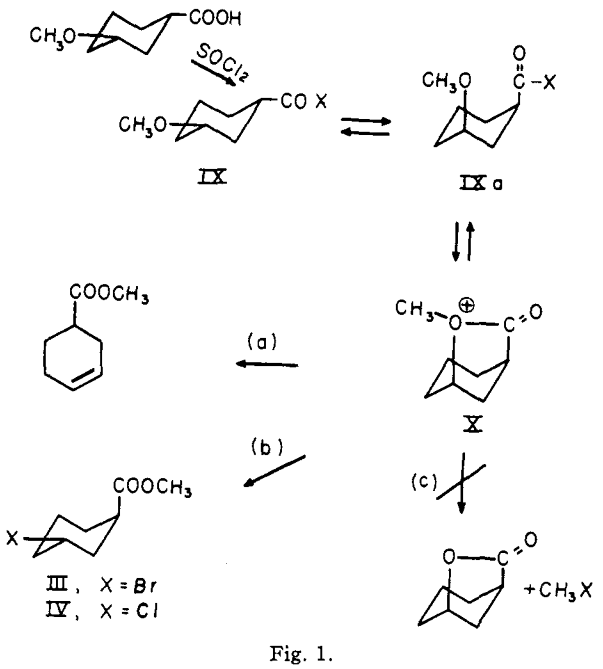
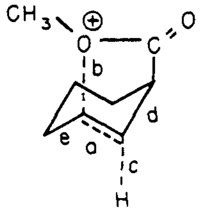


Fig. 1.

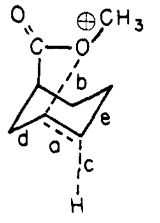
It is first instructive to consider the competitive formation of the unsaturated ester. In the present cases, there is a greater proportion of unsaturated ester formed than was reported by Wiberg or Prelog. This is undoubtedly due to the fact that in the intermediate X, the planar four-center arrangement favorable to elimination is appropriately locked in place. This makes it possible for elimination to compete favorably on an energetic basis with further substitution.

The preference for elimination of the 4-hydrogen over the 2-hydrogen warrants further comment. Examination of the postulated transition state XI leading to methyl 2-cyclohexene-1-carboxylate (XII) reveals that as the double bond (a) is forming and bonds (b) and (c) are breaking, bonds (a), (d) and (e) must be rotated into coplanarity. These three events may be difficult to coördinate since (d) and (e) cannot be rotated a great deal until (b) is broken—*i.e.*, in order to rotate (d) into the (a)(e) plane the carbomethoxy group must be moved rather far from carbon-3.

In the postulated transition state (XIII) leading to methyl 3-cyclohexene-1-carboxylate (V), as the double bond (a) is forming and bonds (b) and (c) are breaking bonds (a), (d) and (e) must be rotated into coplanarity. The three events occurring in this transition state can be more easily coördinated since the carbomethoxy group formed is one carbon farther removed from the developing double bond. Furthermore, an investigation of a Fisher–Hirshfelder–Taylor model of V shows that the centers of the methoxyl oxygen and the center of the carbon-3, when in the conformation permitting their closest approach, are about 3.5 Å. apart. The corresponding distance in XII is about 4.0 Å. Therefore, at the instant bond (b) is broken, the conformation of the distorted XII will be at a higher energy than the distorted V by an amount related to the 0.5 Å. difference between the methoxyl oxygen and carbon-3 in the conformations pictured above. This energy difference will be reflected in their transition states.



XI



XIII

It is further to be noted that the ionization of X to the ring carbonium ion is not consistent with the facts since it has been shown[11] that methyl *cis*-3-tosyloxycyclohexanecarboxylate (XV) undergoes normal solvolysis and elimination. The products of elimination resulting from XV are V and XII, with V predominating.

It is thus clear that the elimination process is synchronous, and that the geometry of the transition state exerts a profound control upon the product formed.

Turning now to the question of the two substitution processes available to the oxonium ion X, it is noteworthy that ring substitution occurs, with no evidence for substitution at the methyl carbon (pathway c above). The preference for reaction at a secondary carbon is not simply explicable upon the basis of SN1 behavior for the following reasons. The examples studied by Prelog and by Heinbach-Juhasz[6] would have been expected on this basis to give a mixture of products. This was not observed. The cleavage of methyl *sec*-butyl ether by acetyl iodide[12] affords 52% methyl iodide and 28% *sec*-butyl iodide. Were the cleavage SN1 in character, the secondary iodide should be the major product. Were the mechanism a normal SN2 displacement the methyl iodide should be more highly favored. It is suggestive at this point to conclude that the mechanism is of the displacement type, but with the effect of the positively charged leaving group being that differences in rate of reactions at primary, secondary and tertiary carbons are minimized or leveled.

Further comparison may be drawn with the displacement reaction accompanying the decomposition of sulfonium salts.[13] Methylethyl-*n*-propylsulfonium hydroxide affords both methanol and

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[11] D. S. Noyce and H. I. Weingarten, forthcoming publication.

[12] P. G. Stevens, THIS JOURNAL, **62**, 1801 (1940).

[13] E. D. Hughes, C. K. Ingold and G. A. Maw, *J. Chem. Soc.*, 2072 (1948).

ethanol,[14,15] while dimethyl-2-phenylethylsulfonium iodide in sodium ethoxide affords more ethyl 2-phenylethyl ether than methyl ethyl ether. These results are consistent with the hypothesis that displacement of oxonium, sulfonium or ammonium groups shows less selectivity than simple SN2 displacement reactions.

In accord with this hypothesis, comparison with the von Braun cyanogen bromide degradation of tertiary amines is instructive. Here the order of reactivity is methyl > ethyl > *n*-propyl > isopropyl.[16] In the case of N-alkyl pyrrolidine derivatives, there appears an accelerating effect involved in attack upon the methylene carbon of the ring. The rate of cleavage of a pyrrolidine ring in the von Braun reaction is approximately equal to the rate of cleavage of a methyl group. The rate of cleavage of the piperidine ring is intermediate between that of ethyl and *n*-propyl groups.

It would thus appear that in reactions involving ring-breaking displacement,[17] increased rates of reaction are observed. This hypothesis then serves to correlate the reactions reported here with the previously observed examples.

Experimental[18]

Preparation of 3-Methoxycyclohexanecarboxylic Acid (II).—*m*-Methoxybenzoic acid, 65 g. (0.43 mole), dissolved in 300 ml. of 95% ethanol, to which 4 g. of platinum oxide was added, was reduced with hydrogen in 30 hours on a Parr low pressure hydrogenator at room temperature.

The catalyst was removed by filtration and most of the ethanol was removed under reduced pressure. The residue was poured into 500 ml. of water, extracted four times with 1:1 ether–pentane and the combined extracts dried over magnesium sulfate. After removal of the solvent the residue was fractionally distilled yielding 24.7 g. (43%) of cyclohexanecarboxylic acid, b.p. 103–104° (5 mm.), and 28.3 g. (40%) of 3-methoxycyclohexanecarboxylic acid, b.p. 140–142° (5 mm.).

Isolation of *cis*-3-Methoxycyclohexanecarboxylic Acid (*cis*-II).—The mixed acids, II, 28.3 g. (0.18 mole), obtained from the reduction of *m*-methoxybenzoic acid were dissolved in a minimum of refluxing *n*-pentane and seeded with *cis*-II. The precipitate obtained was recrystallized three times from *n*-pentane yielding 8.0 g. of *cis*-II, m.p. 51–52°. An additional 8.3 g. of *cis*-II, m.p. 51–52°, was obtained by continued fractional crystallization of the combined filtrates, a recovery of 60% from the mixed isomers.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.6; H, 8.9.

Rearrangement of *cis*-3-Methoxycyclohexanecarboxylic Acid (*cis*-II) in Thionyl Chloride.—To 10 g. (0.063 mole) of *cis*-II was added 15 g. (0.13 mole) of thionyl chloride. After the initial reaction subsided the resulting solution was heated under reflux on a steam-bath for two hours. The excess thionyl chloride was then removed by several distillations with benzene at reduced pressure. The residue was taken up in additional benzene and washed with sodium carbonate solution and then with water. After drying the benzene solution over magnesium sulfate and evaporating, the residue was fractionally distilled to give two main fractions. Fraction A afforded 2.4 g. (28%) of methyl 3-cyclohexene-1-carboxylate (V), b.p. 82–83° (26 mm.), $n^{25}\mathrm{D}$ 1.4584. V was refractionated for analysis.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.1; H, 8.8.

Fraction B, 5.7 g. (51%), b.p. 117° (22 mm.), $n^{25}\mathrm{D}$ 1.4689, was methyl *trans*-3-chlorocyclohexanecarboxylate (IV). IV was refractionated for analysis.

Anal. Calcd. for $C_8H_{13}O_2Cl$: C, 54.4; H, 7.4; Cl, 20.0. Found: C, 54.4; H, 7.5; Cl, 19.9.

Hydrolysis of (IV).—A solution of 25 ml. of water and 20 ml. of dioxane containing 3.5 g. (0.02 mole) of IV and 2.5 ml. of concd. sulfuric acid was heated on a steam-bath overnight, then poured into 100 ml. of water and extracted with 1:1 ether–pentane. After drying the extracts over magnesium sulfate and removing the solvent, the residue was fractionally distilled yielding 1.35 g. (40%) of acidic material, b.p. 133° (5 mm.). This acidic material, which slowly solidified, was recrystallized two times from *n*-pentane at 0° and 0.4 g. of *trans*-3-chlorocyclohexanecarboxylic acid, m.p. 49.5–51.5°, was obtained.

Anal. Calcd. for $C_7H_{11}O_2Cl$: C, 51.7; H, 6.8; Cl, 21.8. Found: C, 51.8; H, 7.0; Cl, 21.6.

The anilide was prepared in the usual manner and after two crystallizations from benzene–pentane it had a melting range of 157.5–157.9°.

Anal. Calcd. for $C_{13}H_{16}ONCl$: C, 65.7; H, 6.8; N, 5.9; Cl, 14.9. Found: C, 65.8; H, 6.6; N, 6.1; Cl, 14.8.

Preparation of the Anilide of *cis*-II.—To 1.3 g. (0.012 mole) of thionyl chloride was added 1.0 g. (0.0063 mole) of *cis*-II and the mixture kept at 40° for one half hour. The thionyl chloride was removed by several distillations with benzene at reduced pressure and the residue was added to 1.3 g. (0.014 mole) of aniline in 20 ml. of benzene. The benzene layer was washed with water, dilute hydrochloric acid, dilute sodium hydroxide and water and then dried over magnesium sulfate. The filtered solution was concentrated to a small volume and cooled causing the precipitation of the anilide of *cis*-3-methoxycyclohexanecarboxylic acid. The anilide was crystallized from benzene–pentane and 0.27 g. (18%) of fine needles were obtained, m.p. 130.5–131.5°.

Anal. Calcd. for $C_{14}H_{19}O_2N$: C, 72.1; H, 8.2; N, 6.0. Found: C, 72.2; H, 8.1; N, 5.9.

Preparation of the Anilide of *trans*-II.—A sample of 4 g. (0.025 mole) of the mixed *cis*-II and *trans*-II acids obtained by concentrating the combined filtrates from which *cis*-II had been removed was added to 6 g. (0.05 mole) of thionyl chloride. This solution was heated on a steam-bath for two hours and then treated as in the above experiment to afford 1.4 g. of the anilide of *trans*-II, m.p. 137.6–138.6°. A mixed melting point with the anilide of *cis*-II depressed to 109–115°.

Anal. Calcd. for $C_{14}H_{19}O_2N$: C, 72.1; H, 8.2; N, 6.0. Found: C, 72.1; H, 8.3; N, 5.8.

Rearrangement of *cis*-3-Methoxycyclohexanecarboxylic Acid (*cis*-II) in Phosphorus Tribromide.—Ten grams (0.063 mole) of *cis*-I was added to 15 g. (0.055) mole of phosphorus tribromide and the mixture was heated on a steam-bath for two hours. At the end of this time the reaction mixture was poured into ice, neutralized with solid sodium carbonate and extracted three times with benzene. The benzene solution was dried and evaporated and methyl *trans*-3-bromocyclohexanecarboxylate (III), 9.75 g. (70%) was obtained upon fractional distillation of the residue, b.p. 129–131° (24 mm.).

A small forerun, 0.5 g., boiling at a temperature corresponding to V was also isolated but was not further characterized.

Preparation of III from the Lactone of *cis*-3-Hydroxycyclohexanecarboxylic Acid.—Gaseous hydrogen bromide was passed into a mixture of 6 g. (0.047 mole) of the lactone of *cis*-3-hydroxycyclohexanecarboxylic acid in 15 ml. of 40% hydrobromic acid until saturated at 0°, then permitted to stand overnight. The resulting solution was poured into water, extracted with 1:2 ether–pentane, dried, evaporated and the product fractionally distilled. The obtained *trans*-3-bromocyclohexanecarboxylic acid, 5.2 g. (35%),

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(14) C. K. Ingold, J. A. Jessop, K. I. Kuriyan and A. M. M. Mandour, *J. Chem. Soc.*, 533 (1933).

(15) C. K. Ingold and K. I. Kuriyan, *ibid.*, 991 (1933).

(16) E. A. Hageman, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 198.

(17) This situation is to be contrasted to the normal displacement or solvolysis which takes place at a ring atom, but with the extra-annular atom leaving, *e.g.*, cyclohexyl chloride.

(18) All melting points are corrected; boiling points are uncorrected. An 18" modified Podbielniak column was used for all fractionations. The infrared spectra were recorded by a Perkin-Elmer model 21 spectrophotometer using 0.1-mm. sodium chloride cells with solutions 0.2 *M* in chloroform. Microanalyses are by the Microanalytical Laboratory, University of California.

b.p. 141–142° (5 mm.), was crystallized once from *n*-pentane, m.p. 64–65° (lit. m.p. 62–63°,[9] m.p. 67–68°[8]).

The bromo acid was dissolved in dry ether and an excess of diazomethane in ether was added. The ether was removed after drying and the residue fractionally distilled yielding 3.5 g. of authentic III, b.p. 120–121° (15 mm.), $n^{25}\text{D}$ 1.4923. Authentic III was characterized by infrared analysis.

Anal. Calcd. for $C_8H_{13}O_2Br$: C, 43.5; H, 5.9; Br, 36.2. Found: C, 43.1; H, 5.9; Br, 36.1.

Isolation of *trans*-3-Methoxycyclohexanecarboxylic Acid (*trans*-II).—Thirteen grams of the mixed acids (*cis*-II and *trans*-II), obtained from the combined filtrates which yielded *cis*-II, was dissolved in 20 g. of thionyl chloride and heated on a steam-bath for two hours. At the end of this time the excess thionyl chloride was removed by distillation with several portions of benzene. The reaction mixture was then poured into water, neutralized with solid sodium carbonate and extracted twice with pentane. The aqueous phase was acidified with hydrochloric acid to a *p*H of 2 and extracted with ether. This solution was dried over magnesium sulfate, evaporated and distilled to give 4.3 g. (33%) of *trans*-II, b.p. 123–125° (2 mm.), $n^{25}\text{D}$ 1.4661.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.8; H, 8.9.

Behavior of Methyl *trans*-3-Chlorocyclohexanecarboxylate (IV) in Thionyl Chloride Rearrangement Conditions.—IV, 4.3 g., was dissolved in 4 g. of thionyl chloride and placed on a steam-bath for two hours. The thionyl chloride was removed by several distillations with benzene and the residue was fractionally distilled yielding 3.8 g. (89%) of IV, b.p. 119–120° (25 mm.).

Preparation of Methyl 4-Methoxycyclohexanecarboxylate.—To a hydrogenation bomb preheated to about 30° was added a warm solution of 50 g. (0.3 mole) of methyl anisate in 50 ml. of absolute ethanol. Commercial Raney nickel, 3–6 g., was added, the bomb mounted on a shaker and the hydrogenation carried out at 170° and 3600 pounds per square inch. The theoretical amount of hydrogen was taken up in four to six hours. After the catalyst was removed by filtration and most of the ethanol removed by low pressure distillation, the residue was fractionated giving two fractions. The first, methyl cyclohexanecarboxylate, weighed 11.2 g. (26%) and had a boiling range of 85–110° (30 mm.). The second, methyl 4-methoxycyclohexanecarboxylate, weighed 29.0 g. (56%) and had a b.p. of 122–124° (30 mm.).

Hydrolysis of Methyl 4-Methoxycyclohexanecarboxylate.—Methyl 4-methoxycyclohexanecarboxylate, 29 g. (0.17 mole), was combined with a solution of 80 ml. of water, 30 ml. of methanol and 23 g. (0.41 mole) of potassium hydroxide. This mixture was heated on a steam-bath for 90 minutes then poured into 200 ml. of water. The aqueous solution was extracted once with *n*-pentane to remove any neutral material then acidified to a *p*H of 2 and extracted three times with 1:1 ether–pentane. The extracts were dried over magnesium sulfate and following the removal of the solvent the residue was fractionally distilled to yield 23.4 g. (90%) 4-methoxycyclohexanecarboxylic acid (VI), b.p. 142° (6 mm.).

Isolation of *cis*-4-Methoxycyclohexanecarboxylic Acid (*cis*-VI).—VI, 23.4 g., was dissolved in ether and then cooled in a Dry Ice-bath. The ether was decanted after precipitation without collecting the precipitate. This process was repeated and following the second crystallization the solid was collected, dried and recrystallized twice from *n*-pentane at room temperature. A sample of *cis*-VI, 7.2 g. (31%), m.p. 54.6–55.6°, was obtained.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.7; H, 8.8.

The anilide of *cis*-VI was prepared in the same way that the anilide of *cis*-II was prepared, m.p. 123.3–124.3°.

Anal. Calcd. for $C_{14}H_{19}O_2N$: C, 72.1; H, 8.2. Found: C, 71.9; H, 7.9.

Isolation of *trans*-4-Methoxycyclohexanecarboxylic Acid (*trans*-VI).—An 8.6-g. sample of V was treated with thionyl chloride in the same process used to isolate *trans*-II. *trans*-VI, 1.65 g. (19%), was obtained and on several crystallizations from *n*-pentane gave a m.p. of 59–60°.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.9; H, 8.8.

The anilide of *trans*-VI was prepared in the usual way and on recrystallization from benzene–pentane had a m.p. of 186.0–186.4°.

Anal. Calcd. for $C_{14}H_{19}O_2N$: C, 72.1; H, 8.2; N, 6.0. Found: C, 72.2; H, 8.1; N, 6.1.

Rearrangement of *cis*-4-Methoxycyclohexanecarboxylic Acid (*cis*-VI) in Thionyl Chloride.—Seven grams (0.044 mole) of *cis*-VI was added to 14 g. (0.12 mole) of thionyl chloride and the solution heated on a steam-bath for 2.5 hours. At the end of this period the thionyl chloride was removed by repeated distillation with benzene and the product was then fractionally distilled. The first fraction proved to be 2.7 g. (44%) of V, b.p. 91° (39 mm.). V was refractionated and an infrared spectrum obtained, which was identical to that of authentic V.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.4; H, 9.1.

The second fraction proved to be methyl *trans*-4-chlorocyclohexanecarboxylate (VII), 2.3 g. (30%), b.p. 119° (20 mm.), $n^{25}\text{D}$ 1.4670. This compound was also characterized by an infrared spectrum.

Anal. Calcd. for $C_8H_{13}O_2Cl$: C, 54.4; H, 7.4; Cl, 20.1. Found: C, 54.2; H, 7.3; Cl, 19.9.

Hydrolysis of VII.—To 40 ml. of 1:1 solution of water–dioxane was added 1.0 g. of VI and 2 ml. of concentrated sulfuric acid. This two-phase mixture was heated on a steam-bath for six hours. The resulting solution was then poured into 70 ml. of water and placed in a refrigerator overnight. The precipitate of *trans*-4-chlorocyclohexanecarboxylic acid was collected and on drying weighed 0.55 g. (61%), m.p. 157–159°. A second crop yielded 0.25 g. (27%). The first crop was crystallized from benzene–pentane giving 0.3 g. of acid having a m.p. of 159.0–159.8°.

Anal. Calcd. for $C_7H_{11}O_2Cl$: C, 51.7; H, 6.8. Found: C, 51.5; H, 6.7.

The anilide was prepared in the usual way, and recrystallized from benzene–pentane, m.p. 196.5–196.8°.

Anal. Calcd. for $C_{13}H_{16}ONCl$: C, 65.7; H, 6.8; N, 5.9; Cl, 14.9. Found: C, 65.4; H, 6.7; N, 6.1; Cl, 14.9.

Rearrangement of *cis*-4-Methoxycyclohexanecarboxylic Acid (*cis*-VI) with Phosphorus Tribromide.—*cis*-VI, 7 g. (0.044 mole), was added to 12 g. (0.044 mole) of phosphorus tribromide and the reaction mixture was heated on a steam-bath for 2.5 hours. The resulting mixture was then poured into water made basic with solid sodium carbonate and extracted with pentane. After drying the pentane extracts over magnesium sulfate and removing the solvent the product was fractionally distilled affording 5.7 g. (59%) of methyl *trans*-4-bromocyclohexanecarboxylate (VIII) b.p. 128–130° (18 mm.), $n^{25}\text{D}$ 1.4916. VII was characterized by an infrared spectrum.

Anal. Calcd. for $C_8H_{13}O_2Br$: C, 43.5; H, 5.9; Br, 36.1. Found: C, 43.8; H, 5.7; Br, 35.5.

The basic aqueous layer was acidified and yielded a precipitate of *trans*-4-bromocyclohexanecarboxylic acid, 1.5 g. (17%) with a melting point range of 160–170°. One crystallization from benzene–pentane raised the melting point to 169–171° (lit.[19] m.p. 167°).

No methyl cyclohexenecarboxylate was detected among the products.

Hydrolysis of VIII.—Four grams of VII was heated under reflux with a 1:1 solution of water-dioxane, 125 ml., containing 8 ml. of concentrated sulfuric acid for four hours. The resulting solution was poured into 150 ml. of water and placed in a refrigerator overnight. The precipitate of *trans*-4-bromocyclohexanecarboxylic acid weighed 0.8 g. (22%) and melted over a wide range to 170°. Three recrystallizations from benzene–pentane gave 0.5 g., m.p. 170.8–171.4° (lit.[19] m.p. 167°).

Anal. Calcd. for $C_7H_{11}O_2Br$: C, 40.6; H, 5.3; Br, 38.6. Found: C, 40.6; H, 5.2; Br, 38.6.

The anilide was prepared in the usual way and was crystallized from benzene–pentane, m.p. 191.0–191.7°.

Anal. Calcd. for $C_{13}H_{16}O_2NBr$: C, 55.3; H, 5.7; N, 5.0; Br, 28.4. Found: C, 55.6; H, 5.7; N, 5.3; Br, 28.4.

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(19) W. H. Perkins, *J. Chem. Soc.*, **85**, 431 (1904).

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]

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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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[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).