phase extracted with ether. After drying over magnesium sulfate, the ether was removed and the residue distilled to afford 78 g. (62%) of product boiling at 155–160° (8 mm.).

Anal. Calcd. for $C_{13}H_{15}Br$: C, 62.1; H, 5.97. Found: C, 62.3; H, 5.82.

2-Methyl-4′-bromobiphenyl.—Dehydrogenation of the olefin described above was accomplished by a method developed by v. Braun, *et al.*,[26] for similar compounds.

To a solution of 50 g. (0.2 mole) of 1-methyl-2-(*p*-bromophenyl)-cyclohexene in 500 ml. of chloroform, kept at 0°, was added 32 g. (0.2 mole) of bromine dropwise. After the addition, the chloroform was distilled off and the residue heated at a bath temperature of 170–180° and at the full vacuum of the oil-pump. Hydrogen and hydrogen bromide were evolved and the substituted biphenyl distilled over. After washing with carbonate and drying over magnesium sulfate the oil was distilled to give 30 g. (63%) of the desired product boiling at 303–306°.[27]

Oxidation of a small quantity of this material with neutral permanganate gave an acid which was cyclized *via* the acid chloride and aluminum chloride to 2-bromofluorenone, m.p. 148–149°.[27]

An attempt at dehydrogenating the olefin with chloranil led to only a very low yield of the biphenyl.

2-Methyl-4′-trimethylsilylbiphenyl.—A mixture of 22 g. (0.089 mole) of 2-methyl-4′-bromobiphenyl and 10.8 g. (0.1 mole) of chlorotrimethylsilane was added dropwise to 5 g. (0.22 g. atom) of sodium sand in 100 ml. of ether. After most of the bromide had been added, the solution began to reflux and the sodium turned dark blue. Refluxing continued spontaneously for 40 minutes. After this, heat was applied and the mixture was refluxed for an additional 3 hours. Working up in the usual manner gave 11 g. (52%) of silane boiling at 295°, which gave a negative Beilstein test for halogen.

Anal. Calcd. for $C_{16}H_{20}Si$: C, 80.0; H, 8.35; Si, 11.66. Found: C, 79.85; H, 8.71; Si, 11.50.

Isolation of Cleavage Products.—A solution of 10 g. (0.044 mole) of 4-trimethylsilylbiphenyl in 150 ml. of the cleaving medium was allowed to stand at room temperature for a week. After pouring into an excess of water, the mixture was extracted thoroughly with ether. After drying over magnesium sulfate, the ether was removed and the residue distilled. There was obtained 2.8 g. (73%) of hexamethylethyldisiloxane, b.p. 98°, $n^{20}\text{D}$ 1.3776, and 4.5 g. (66%) of biphenyl, b.p. 253–256°, m.p. 70°.

Trimethyl-1-naphthylsilane was prepared by the method described by Gilman and co-workers[28]; b.p. 115–116° (1 mm.), $n^{20}\text{D}$ 1.5806, d^{20}_4 0.981; *MR*D (calcd.) 67.40, *MR*D (found) 67.60.

Trimethyl-2-naphthylsilane was prepared from 2-naphthyllithium and trimethylchlorosilane; b.p. 93–95° (0.5 mm.), $n^{20}\text{D}$ 1.5613, d^{20}_4 0.968; *MR*D (calcd.) 67.40, *MR*D (found) 67.08.

Anal. Calcd. for $C_{13}H_{16}Si$: Si, 14.02. Found: Si, 13.63.

Dimethylethylphenylsilane.—Over a period of 4 hours 150 ml. of anhydrous ether containing phenylmagnesium bromide (from 19.5 g. (0.8 g. atom) of magnesium and 73.5 ml. (0.7 mole) of bromobenzene) was added to 103 g. (0.8 mole) of dimethyldichlorosilane. This mixture was heated to reflux during this addition. The ether was then distilled off and the residue refluxed overnight. Approximately 0.9 mole of ethereal ethylmagnesium bromide was added, and the solution again was refluxed overnight.

The product was hydrolyzed with water and worked up in the usual fashion. It was distilled through a Todd continuous wire spiral column and 19 g. of a middle cut was collected for the kinetic work; b.p. 195°, $n^{20}\text{D}$ 1.4938, d^{20}, 0.878; *MR*D (calcd.) 54.73, *MR*D (found) 54.47. The compound was reported previously,[29] and these constants given: $n^{20}\text{D}$ 1.4928, d^{20}_4 0.877.

Anal. Calcd. for $C_{10}H_{16}Si$: C, 73.09; H, 9.28. Found: C, 73.10, 73.08; H, 9.89, 9.98.

Triethylphenylsilane was prepared from ethylmagnesium bromide and phenyltrichlorosilane in the usual manner. The sample used for the kinetic studies had b.p. 73° (1 mm.), $n^{20}\text{D}$ 1.5025, d^{20}_4 0.893; *MR*D (calcd.) 63.96, *MR*D (found) 63.63. The compound was reported previously[29] with the constants $n^{20}\text{D}$ 1.5024, d^{20}_4 0.891.

Triisopropylphenylsilane was prepared from phenyltrichlorosilane and isopropyllithium. The sample used for kinetic studies had b.p. 95° (4 mm.), $n^{20}\text{D}$ 1.5104, d^{20}_4 0.904. The reported[30] constants were $n^{20}\text{D}$ 1.5105, d^{20}_4 0.905.

Acknowledgment.—The authors are grateful to the Ethyl Corporation and the National Science Foundation whose financial assistance made this work possible.

LAFAYETTE, IND.

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[26] J. V. Braun, G. Irmisch and J. Nelles, *Ber.*, **66B**, 1471 (1933).

[27] M. Gomberg and J. Pernert, THIS JOURNAL, **48**, 1372 (1926), report a b.p. of 303–305° for 2-methyl-4′-bromobiphenyl prepared by a diazo coupling method. They converted this material to 2-bromofluorenone, m.p. 149°.

[28] H. Gilman, R. A. Benkeser and G. E. Dunn, THIS JOURNAL, **72**, 1689 (1950).

[29] A. Bygden, Uppsala Dissertation, Sweden, 1916; *C. A.*, **14**, 1974 (1920).

[30] H. Gilman and R. N. Clark, THIS JOURNAL, **69**, 1499 (1947).

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

The Stereochemistry of the Conversion of Organic Chlorides to Acids by Carbonation of the Grignard Reagents[1]

BY HARLAN L. GOERING AND FRED H. MCCARRON[2]

RECEIVED NOVEMBER 4, 1957

The stereochemistry of the conversion of (a) optically active 3,3-dimethylcyclohexyl chloride, (b) *cis*-(Ia) and *trans*-3-methylcyclohexyl chloride (Ib) and (c) *cis*-(IIIa) and *trans*-5-methyl-2-cyclohexenyl chloride (IIIb) to acids by carbonation of the Grignard reagents has been examined. Under the mildest conditions that the chlorides could be converted to the Grignard reagents (refluxing ether) no stereospecificity was observed with any of these three cyclic systems. The optically active system gave completely racemic acid and in the other two systems, epimers gave products having the same configurational composition. The 3-methylcyclohexanecarboxylic acid derived from the 3-methylcyclohexyl chlorides contained 26% of the *trans* isomer and the acid derived from the 5-methyl-2-cyclohexenyl chlorides contained 68% of the *trans* isomer.

There is considerable evidence that the two-step conversions of alkyl halides to various products *via* the Grignard reagents are non-stereospecific, *i.e.*, enantiomeric and epimeric halides give the same product. It has been found in several cases that optically active halides in which the halogen atom

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[2] Shell Oil Co. Fellow 1955–1956.

is attached to the only asymmetric center give completely racemic products.[3] It also has been found that cholestanyl and epicholestanyl bromide are converted to the same acid, cholestane-3β-carboxylic acid, by carbonation of the Grignard reagents.[4] The loss of configuration in such processes is apparently consistent with the observation of Letsinger[5] that optically active 1-methylheptyllithium can be prepared at −70° but racemizes rapidly when the temperature is raised to 0°.

In contrast to the above observations Mousseron and co-workers have repeatedly claimed[6] that carbonation of the Grignard reagents derived from the isomeric 3-methylcyclohexyl chlorides and bromides gives 3-methylcyclohexanecarboxylic acid with predominant retention of configuration. It also has been reported[7] that the epimeric *trans*-2-chlorodecalins are stereospecifically converted to the epimeric *trans*-2-decanols by oxidation of the Grignard reagents. Because of these conflicting reports we have carefully examined the stereochemistry of the conversion of chlorides to acids by carbonation of the Grignard reagents in three cyclic systems. The chlorides used in the present work were (a) (−)-3,3-dimethylcyclohexyl chloride, (b) *cis*-(Ia) and *trans*-3-methylcyclohexyl chloride (Ib) and (c) *cis*-(IIIa) and *trans*-5-methyl-2-cyclohexenyl chloride (IIIb).

The Conversion of Optically Active 3,3-Dimethylcyclohexyl Chloride to 3,3-Dimethylcyclohexanecarboxylic Acid.—Optically active 3,3-dimethylcyclohexyl chloride, $[\alpha]^{24}\mathrm{D}$ −2.37°, was prepared from active 3,3-dimethylcyclohexanol, $[\alpha]^{25}\mathrm{D}$ 1.13°, by treatment with phosphorus pentachloride.[8] The chloride was converted to the Grignard reagent[9] which was poured onto Dry Ice. A 37% yield of apparently pure 3,3-dimethylcyclohexanecarboxylic acid, $[\alpha]^{25}\mathrm{D}$ $-0.011 \pm 0.002°$, was isolated from the reaction. The product was identified by its chemical composition and neutral equivalent and conversion to the known[10] 3,3-dimethylcyclohexylcarbinol by reduction with lithium aluminum hydride. That the trace of activity observed in the product was not due to active 3,3-dimethylcyclohexanecarboxylic acid was demonstrated in the following manner. Reduction of (+)-3,3-dimethylcyclohexanecarboxylic acid, $[\alpha]^{26}\mathrm{D}$ 1.14°, with lithium aluminum hydride was found to give (+)-3,3-dimethylcyclohexylcarbinol, $[\alpha]^{24}\mathrm{D}$ 2.07°, *i.e.*, this conversion results in about a twofold increase in rotation. When the same reduction was applied to the product from the Grignard reaction the resulting 3,3-dimethylcyclohexylcarbinol was completely inactive. Thus the conversion of the chloride to the acid in this optically active cyclic system is non-stereospecific.

Carbonation of the Grignard Reagents Derived from *cis*- and *trans*-3-Methylcyclohexyl Chloride.—The isomeric 3-methylcyclohexyl chlorides were prepared by the reaction of the isomeric 3-methylcyclohexanols[11] with phosphorus pentachloride in chloroform. It has been shown previously that this reaction is stereospecific—optically active alcohols give active chlorides[8] and epimeric chlorides give different products[12]—and different products were indeed obtained from the isomeric 3-methylcyclohexanols. If it is assumed that the reaction involves inversion of configuration, as is evidently the case in other systems,[12,13] the *trans*-chloride Ib is obtained from the *cis*-alcohol and the *cis*-chloride Ia is obtained from the *trans*-alcohol. It is noteworthy that the relative physical properties (indices of refraction and densities) are consistent with this assignment of configuration.[14] The infrared spectra of the two products were significantly different. The spectrum of the chloride derived from the *cis*-alcohol had characteristic bands at 9.01, 10.42, 12.95 and 14.68 μ and the spectrum of the chloride derived from the *trans*-alcohol had characteristic bands at 7.48, 11.12, 10.62, 12.38 and 12.78 μ. Slight absorption in the spectrum of each isomer corresponding to the strong characteristic bands in the spectrum of the other indicated a slight amount of intercontamination. When samples of the two chlorides were carefully fractionated with an efficient all-glass column the spectra of the successive fractions showed only minor changes indicating that both isomers were essentially homogeneous. Careful study of the spectra indicated that the upper limits for intercontamination were 5% for the chloride derived from the *trans*-alcohol and 3% for the chloride derived from the *cis*-chloride.

The isomeric chlorides were converted to 3-methylcyclohexanecarboxylic acid by carbonation of the Grignard reagents[9] and the products were isolated and purified in such a way as to avoid fractionation or isomerization (equilibration) of the isomeric 3-methylcyclohexanecarboxylic acids (II). The infrared spectra of the products derived from the isomeric chlorides were indistinguishable. Authentic *cis*-(IIa)[15] and *trans*-3-methylcyclohexanecarboxylic acid (IIb)[16] were prepared for comparison purposes and the spectra for these compounds were found to differ considerably. The pure isomeric acids were isolated and purified in the same way as the products from the Grignard reagents without isomerization. That the products isolated from the Grignard reaction were uncontaminated binary mixtures of IIa and IIb was shown by neutral equivalents, carbon–hydrogen analysis and infrared spectra. The infrared spec-

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[3] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); C. W. Porter, THIS JOURNAL, **57**, 1436 (1935); A. M. Schwartz and J. R. Johnson, *ibid.*, **53**, 1063 (1931).

[4] G. Roberts and C. W. Shoppee, *J. Chem. Soc.*, 3418 (1954).

[5] R. L. Letsinger, THIS JOURNAL, **72**, 4842 (1950).

[6] M. Mousseron and R. Jacquier, *Bull. soc. chim. France*, C80 (1951), and references cited therein.

[7] A. Zlatkis and E. A. Smith, *Can. J. Chem.*, **29**, 162 (1951).

[8] H. L. Goering and F. H. McCarron, THIS JOURNAL, **78**, 2270 (1956).

[9] The Grignard reagents were prepared at the temperature of refluxing ether. Attempts to prepare the reagents at lower temperatures were unsuccessful.

[10] W. E. Doering and F. M. Beringer, THIS JOURNAL, **71**, 2221 (1949).

[11] H. L. Goering and C. Serres, *ibid.*, **74**, 5908 (1952).

[12] R. J. Bridgewater and C. W. Shoppee, *J. Chem. Soc.*, 1709 (1953); C. W. Shoppee and G. H. R. Summers, *ibid.*, 1790 (1952).

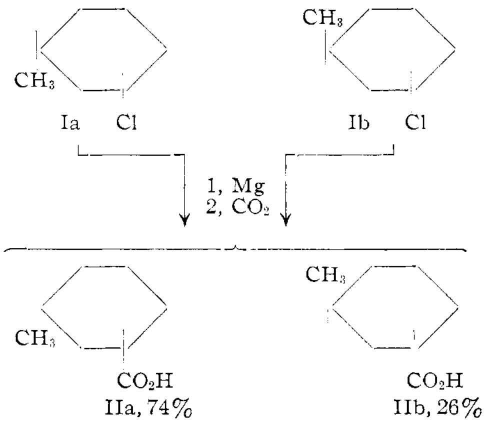
[13] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *ibid.*, 1252 (1937); W. Gerrard and R. J. Phillips, *Chemistry & Industry*, 540 (1952); E. D. Hughes, C. K. Ingold and I. C. Whitfield, *Nature*, **147**, 206 (1941).

[14] See N. L. Allinger, *Experientia*, **10**, 328 (1954).

[15] D. S. Noyce and R. J. Nagle, THIS JOURNAL, **75**, 127 (1953).

[16] F. R. Hewgill, P. R. Jefferies and A. K. Macbeth, *J. Chem. Soc.*, 699 (1954).

tra were an exact composite of the spectra for IIa and IIb and showed that the product contained 26 ± 5% of the *trans*-acid IIb. The results of these experiments are summarized below.

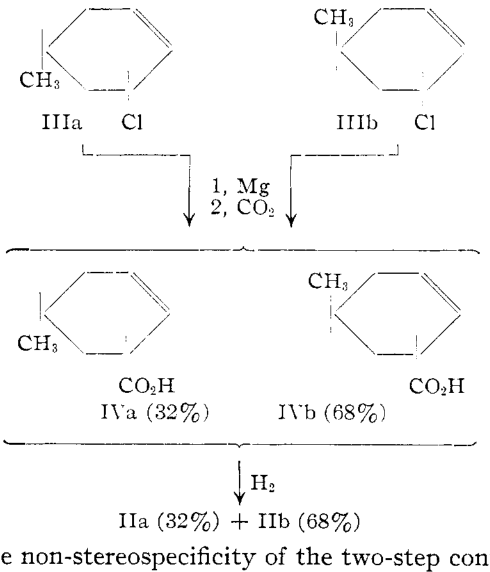


The present results clearly show that contrary to the reports of Mousseron and co-workers,[6] the conversion of the isomeric 3-methylcyclohexyl chlorides (I) to 3-methylcyclohexanecarboxylic acid (II) by carbonation of the Grignard reagent is not stereospecific. There are several possible reasons for the apparent stereospecificity observed by Mousseron and co-workers. Comparison of physical properties[17] clearly shows that the chlorides used in the present work differed from those used previously. It has been shown[18] that the acid obtained by carbonation of the Grignard reagent derived from the chloride prepared by the reaction of hydrochloric acid with 3-methylcyclohexanol, the method used by Mousseron and co-workers to prepare one of the chlorides, contains considerable quantities of *trans*-4-methylcyclohexanecarboxylic acid. Thus it seems almost certain that at least one of the "isomeric" acids obtained by Mousseron and co-workers was contaminated with 4-methylcyclohexanecarboxylic acid. The analytical method[19] used to determine the configurational compositions of the 3-methylcyclohexanecarboxylic acids would not detect the presence of 4-methylcyclohexanecarboxylic acid. This method involved esterification and then fractionation of the methyl esters which are reported[19] to boil 2° apart. The refractive indices of the supposedly isomeric acids obtained by saponification of the "separated" methyl esters were nearly identical and considerably lower than that observed in the present work for the isomer (*cis*) with the lowest refractive index.

As already has been suggested[20] it appears likely that the apparent stereospecificity reported for the conversion of the isomeric *trans*-2-chlorodecalins to the isomeric *trans*-2-decanols can be explained by the likelihood that one of the isomeric chlorides contained 1-chlorodecalin and thus one of the products was largely a mixture of the isomeric *trans*-1-decanols.

Carbonation of the Grignard Reagents Derived from *cis*-(IIIa) and *trans*-5-Methyl-2-cyclohexenyl Chloride (IIIb).—The Grignard reagents were prepared[9] from pure samples of *cis*-(IIIa) and *trans*-5-methyl-2-cyclohexenyl chloride (IIIb)[21] using a high ratio of magnesium to allylic chloride in dilute ether solution.[22] After carbonation and hydrolysis the ether solutions of the products were hydrogenated (platinum oxide) to convert the unknown isomeric 5-methyl-2-cyclohexenecarboxylic acids (IV) to the known isomeric 3-methylcyclohexanecarboxylic acids (II). In each experiment, an amount of hydrogen equivalent to the amount of allylic halide used in the reaction was absorbed. Thus the unsaturated acid as well as the coupling product was reduced completely and the configurational composition of the saturated acid II was the same as that of the unsaturated acid IV. The saturated acid was isolated in 15% yield from the *trans*-chloride IIIb and 37% yield from the *cis*-chloride IIIa in such a way as to avoid fractionation of the isomers. A 55% yield of the hydrogenated coupling product, 3,3′-dimethylbicyclohexane, was isolated from the experiment involving the *trans*-chloride IIIb.

The configurational composition of the 3-methylcyclohexanecarboxylic acids was determined as described in the preceding section. The infrared spectra of the products derived from the isomeric chlorides were indistinguishable and corresponded in detail to a composite of the spectra of pure *cis*-(IIa) and *trans*-3-methylcyclohexanecarboxylic acid (IIb). Neutral equivalents and physical properties as well as infrared spectra indicated the products were pure binary mixtures of IIa and IIb. Infrared analysis showed that the products contained 68 ± 5% of the *trans*-acid. These conversions are summarized below.



The non-stereospecificity of the two-step conversion of 5-methyl-2-cyclohexenyl chloride (III) to 5-methyl-2-cyclohexenecarboxylic acid (IV) does not appear to be a result of isomerization (equilibration)

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[17] M. Mousseron, R. Granger and J. Valette, *Bull. soc. chim. France*, 244 (1946).

[18] L. H. Darling, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 1364 (1953).

[19] M. Mousseron, *Bull. soc. chim. France*, 605 (1947).

[20] W. G. Dauben and R. C. Tweit, THIS JOURNAL, **76**, 3197 (1954).

[21] (a) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 4042 (1955); (b) the pure samples of the isomeric 5-methyl-2-cyclohexenyl chloride were supplied by Dr. E. F. Silversmith.

[22] W. G. Young and M. Eisner, THIS JOURNAL, **63**, 2113 (1941).

of the reactants (III) or products (IV). *trans*-5-Methyl-2-cyclohexenyl chloride (IIIb) (the most reactive isomer)[21] does not isomerize to a detectable extent (2%) when allowed to stand at the reaction temperature for four hours (the time required for the reaction). As mentioned in the preceding section the saturated acid II is not isomerized or fractionated under the conditions of the reaction and there is little doubt but that IV is also stable under these conditions.

The ultraviolet spectrum of the ether solution of the carbonation product was examined prior to reduction to determine if the β,γ-unsaturated acid (IV) was isomerized to the α,β-unsaturated acid, 5-methyl-1-cyclohexenecarboxylic acid, under the conditions of the reaction. If indeed such an isomerization occurred both allylic halides would necessarily give the same final product. From the absorption at 205 μ—crotonic acid is reported[23] to have an extinction coefficient of 10^4 at this wave length—it was established that IV obtained by carbonation contains little ($<5\%$) if any of the α,β-unsaturated isomer. These results parallel those of Young and co-workers[24] who have shown that pure β,γ-unsaturated acids are obtained by carbonation of Grignard reagents derived from allylic halides.

From the present work it is clear that intermediates or equilibria common to the two diastereoisomers (four optical isomers) are involved at some stage during the two step process.

Experimental[25]

Materials.—*dl*-3,3-Dimethylcyclohexyl chloride, b.p. 67–69° (25 mm.), $n^{25}\mathrm{D}$ 1.4586 (lit.[8] b.p. 70° (24 mm.), $n^{25}\mathrm{D}$ 1.4588), and (−)-3,3-dimethylcyclohexyl chloride, b.p. 49–52° (8 mm.), $n^{25}\mathrm{D}$ 1.4583, $[\alpha]^{24}\mathrm{D}$ −2.37° (neat) (lit.[8] b.p. 49.4–50° (8 mm.), $n^{25}\mathrm{D}$ 1.4580, $[\alpha]^{24}\mathrm{D}$ −2.37° (neat), were prepared from *dl*-3,3-dimethylcyclohexanol[10] by the previously described procedure.[8]

The *cis*- and *trans*-5-methyl-2-cyclohexenyl chloride[21] used in the present work were shown to be configurationally homogeneous by comparison of their infrared spectra with those of authentic samples.

cis-3-Methylcyclohexanecarboxylic acid,[15] b.p. 78° (0.04 mm.), $n^{25}\mathrm{D}$ 1.4557, amide m.p. 158.5–159.7° (lit.[15] b.p. 133–134° (14.5 mm.), $n^{21}\mathrm{D}$ 1.4571, amide m.p. 158–158.8°), and *trans*-3-methylcyclohexanecarboxylic acid,[16] b.p. 81–82° (0.04 mm.), $n^{25}\mathrm{D}$ 1.4597, anilide m.p. 124.8–125.4° (lit.[16] b.p. 92° (1.3 mm.), $n^{20}\mathrm{D}$ 1.4618, anilide m.p. 123°), were prepared by published procedures.

***cis*-3-Methylcyclohexyl Chloride.**—Treatment of 27 g. (0.23 mole) of *trans*-3-methylcyclohexanol, b.p. 69.8–70° (14 mm.), $n^{25}\mathrm{D}$ 1.4575, *p*-nitrobenzoate m.p. 62.6–63.2° (lit.[26] b.p. 64–65° (11 mm.), $n^{25}\mathrm{D}$ 1.4571, *p*-nitrobenzoate m.p. 62.8–63.0°), with phosphorus pentachloride as described previously[8] gave 11 g. (36%) of *cis*-3-methylcyclohexyl chloride, b.p. 63–68° (29 mm.), and 14 g. (35%) of material, b.p. 79–92° (29 mm.), assumed to be a mixture of isomeric 1,2-dichloro-3-methylcyclohexanes and 1,2-dichloro-4-methylcyclohexanes.[8] After redistillation the *cis*-3-methylcyclohexyl chloride had: b.p. 60.5–60.8° (29 mm.), $n^{25}\mathrm{D}$ 1.4543, d^{25}_{4} 0.950, *M*D 37.8 (calcd. 37.2).

Anal. Calcd. for $C_7H_{13}Cl$: Cl, 26.73. Found: Cl, 26.77.

***trans*-3-Methylcyclohexyl Chloride.**—Treatment of 89 g. (0.78 mole) of *cis*-3-methylcyclohexanol, b.p. 73–74° (12 mm.), $n^{25}\mathrm{D}$ 1.4560, *p*-nitrobenzoate, m.p. 56.8–57.4°, acid phthalate m.p. 94.4–94.9° (lit. b.p. 68–70° (15 mm.),[25] $n^{25}\mathrm{D}$ 1.4556,[26] *p*-nitrobenzoate m.p. 56.4–57.2°,[11] acid phthalate m.p. 94°),[27] with phosphorus pentachloride gave 82 g. (78%) of *trans*-3-methylcyclohexyl chloride, b.p. 46–49° (15 mm.), and 15 g. (11%) of material, b.p. 74–77° (16 mm.), assumed to be a mixture of isomeric 1,2-dichloro-3-methylcyclohexanes and 1,2-dichloro-4-methylcyclohexanes.[8] After redistillation, the *trans*-3-methylcyclohexyl chloride had: b.p. 43.8–44.0° (14 mm.), $n^{25}\mathrm{D}$ 1.4565, d^{25}_{4} 0.980, *M*D 36.8 (calcd. 37.2).

Anal. Calcd. for $C_7H_{13}Cl$: Cl, 26.73. Found: Cl, 27.02.

Grignard Reactions. A. (***dl*-3,3-Dimethylcyclohexyl Chloride**).—To 2.5 g. (0.10 mole) of magnesium was added 2 ml. of a solution of 14 g. (0.093 mole) of *dl*-3,3-dimethylcyclohexyl chloride in 50 ml. of anhydrous ether. Two drops of methyl iodide were added and the mixture was refluxed for 10 min.; 25 ml. of anhydrous ether was added after which the rest of the halide solution was added dropwise. The addition of the halide solution required about 0.5 hour. After refluxing for 0.5 hour the Grignard reagent was carbonated by the method of Hussey.[28] The resulting mixture was hydrolyzed with dilute hydrochloric acid. The ether layer was separated, and the aqueous layer extracted four times with ether. The combined ether extracts were extracted with four 25-ml. portions of 10% sodium hydroxide. The basic layer was acidified (congo red) with hydrochloric acid and extracted four times with chloroform. After distillation of the chloroform, the residue was distilled to give 6.3 g. (44%) of *dl*-3,3-dimethylcyclohexanecarboxylic acid, b.p. 103–108° (0.9 mm.), $n^{25}\mathrm{D}$ 1.4573, d^{25}_{4} 0.987, neut. equiv. 157.7 (calcd. 156.2), *M*R 43.8 (calcd. 43.1).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.35; H, 10.43.

The acid was converted[29] to *p*-phenylphenacyl 3,3-dimethylcyclohexanecarboxylate which melted at 105.2–106.2° (aqueous ethanol).

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48. Found: C, 78.89; H, 7.45.

B. (**(−)-3,3-Dimethylcyclohexyl Chloride**).—Treatment of 8.3 g. (0.057 mole) of (−)-3,3-dimethylcyclohexyl chloride, $[\alpha]^{24}\mathrm{D}$ −2.37° (neat), and 1.5 g. (0.062 mole) of magnesium under the same conditions as in Part A gave 3.2 g. (37%) of 3,3-dimethylcyclohexanecarboxylic acid, b.p. 106–110° (0.7 mm.), $n^{25}\mathrm{D}$ 1.4579, $[\alpha]^{25}\mathrm{D}$ −0.011° (*l* 1 dm., neat). Reduction of this product with lithium aluminum hydride resulted in complete loss of optical activity. This demonstrates that the small observed optical activity was not due to the presence of active 3,3-dimethylcyclohexanecarboxylic acid because reduction of active acid results in an increase in rotation (see below).

C. (***trans*-3-Methylcyclohexyl Chloride**).—Treatment of 9.3 g. (0.07 mole) of *trans*-3-methylcyclohexyl chloride with 1.87 g. (0.077 mole) of magnesium under the same conditions as in Part A gave 4.8 g. (48%) of 3-methylcyclohexanecarboxylic acid (II), b.p. 90–92° (0.45 mm.), $n^{25}\mathrm{D}$ 1.4566, neut. equiv. 142.7 (calcd. 142.2). The infrared spectrum and the carbon–hydrogen analyses corresponded to II.

D. (***cis*-3-Methylcyclohexyl Chloride**).—Treatment of 6.1 g. (0.044 mole) of *cis*-3-methylcyclohexyl chloride with 1.2 g. (0.048 mole) of magnesium under the same conditions as in Part A gave 3.1 g. (50%) of 3-methylcyclohexanecarboxylic acid, b.p. 83–84° (0.12 mm.), $n^{25}\mathrm{D}$ 1.4566, neut. equiv. 142.1 (calcd. 142.2). The infrared spectrum of this product was indistinguishable from that of the product obtained from the *trans*-chloride. The carbon–hydrogen analysis indicated the product was pure II.

E. (***trans*-5-Methyl-2-cyclohexenyl Chloride**).—To 20.4 g. (0.85 mole) of magnesium was added 1 ml. of a solution of 7.3 g. (0.056 mole) of *trans*-5-methyl-2-cyclohexenyl chloride in 100 ml. of anhydrous ether. As soon as the reaction had started, 100 ml. of anhydrous ether was added to the reaction, and the rest of the halide solution added over a period of 4 hr. at room temperature (32–34°). At the end of the addition, the solution was carbonated by the method of Hussey.[28] The resulting mixture was hydrolyzed by adding cold saturated ammonium chloride until a clear

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(23) E. A. Braude, *Ann. Repts. Progr. Chem.*, **42**, 105 (1945).

(24) J. F. Lane, J. D. Roberts and W. G. Young, THIS JOURNAL, **66**, 543 (1944); J. D. Roberts and W. G. Young, *ibid.*, **67**, 148 (1945).

(25) All melting points are corrected.

(26) H. L. Goering and J. P. Blanchard, THIS JOURNAL, **76**, 5405 (1954).

(27) A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 709 (1945).

(28) A. S. Hussey, THIS JOURNAL, **73**, 1364 (1951).

(29) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1946, p. 185.

solution was formed.[24] After acidification with cold dilute hydrochloric acid, the aqueous layer was separated and extracted four times with ether. The combined ether solution was washed with saturated sodium chloride and dried over magnesium sulfate. The ethereal solution was concentrated to a volume of 200 ml. and hydrogenated at room temperature and 40 lb. pressure with 0.8 g. of platinum oxide catalyst. Within a few minutes 96% of the theoretical amount of hydrogen was absorbed.

After removal of the catalyst by filtration, the ether solution was extracted with 100 ml. of cold 10% sodium hydroxide in four portions. The aqueous layer was acidified to congo red with cold hydrochloric acid and extracted four times with chloroform. The chloroform was distilled and by distillation of the residue a 1.2 g. (15%) yield of 3-methylcyclohexanecarboxylic acid, b.p. 79–80° (0.04 mm.), $n^{25}\mathrm{D}$ 1.4583, neut. equiv. 142.3 (calcd. 142.2), was obtained. The infrared spectrum of this product corresponded in detail to a composite of the spectra of the isomeric 3-methylcyclohexanecarboxylic acids.

The ether solution from which the acid was extracted was washed once with saturated sodium chloride and dried over potassium carbonate. The ether was distilled and distillation of the residue gave 3.6 g. (55%) of 3,3′-dimethylbicyclohexane, b.p. 140–145° (29 mm.), $n^{25}\mathrm{D}$ 1.4746, d^{25}_{4} 0.872, $M\mathrm{D}$ 62.7 (calcd. 62.6).

Anal. Calcd. for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.33; H, 13.47.

The infrared spectrum of this material had bands at 3.15 μ (carbon–hydrogen bond), 6.90 μ (carbon–carbon bond) and 7.25 μ (terminal methyl group). This product arises from coupling during the Grignard reaction and is presumably a mixture of all or some of the six possible diastereoisomers.

F. (***cis*-5-Methyl-2-cyclohexenyl Chloride**).—When 8.0 g. (0.061 mole) of *cis*-5-methyl-2-cyclohexenyl chloride and 22.4 g. (0.92 atom) of magnesium was treated under the same conditions as Part E, 103% of the theoretical amount of hydrogen was absorbed, and a 3.2 g. (37%) yield of 3-methylcyclohexanecarboxylic acid, b.p. 81–82° (0.09 mm.), $n^{25}\mathrm{D}$ 1.4583, neut. equiv. 142.3 (calcd. 142.2) was obtained. The infrared spectrum of this product was indistinguishable from that of the product derived from the *trans*-chloride and corresponded in detail to that of a binary mixture of IIa and IIb.

Lithium Aluminum Hydride Reduction of 3,3-Dimethylcyclohexanecarboxylic Acid. A. 3,3-Dimethylcyclohexanecarboxylic Acid from Grignard Reaction.—An ethereal solution of 1.75 g. (0.011 mole) of the 3,3-dimethylcyclohexanecarboxylic acid, $[\alpha]^{25}\mathrm{D}$ −0.011° (*l* 1 dm., neat), obtained by carbonation of the Grignard reagent derived from (−)-3,3-dimethylcyclohexyl chloride, $[\alpha]^{24}\mathrm{D}$ −2.37° (*l* 1 dm., neat) was added to a solution of 1.5 g. (0.04 mole) of lithium aluminum hydride in 30 ml. of anhydrous ether. The resulting mixture was hydrolyzed with 5% hydrochloric acid, and the aqueous phase was extracted with ether. After removal of the ether 1.2 g. (77%) of inactive 3,3-dimethylcyclohexylcarbinol, b.p. 89° (10 mm.), $n^{25}\mathrm{D}$ 1.4598, 3-nitrophthalate m.p. 203.4–204.4° (lit.[10] b.p. 89–92° (8 mm.), 3-nitrophthalate m.p. 200.5–202.5°), was obtained. The melting point of authentic 3-nitrophthalate, m.p. 203.8–204.6° (prepared by the method of Doering and Beringer[10]), was not depressed when mixed with the 3-nitrophthalate from the above reduction.

B. Optically Active 3,3-Dimethylcyclohexanecarboxylic Acid.—*dl*-3,3-Dimethylcyclohexanecarboxylic acid was resolved by dissolving 31.2 g. (0.2 mole) of inactive acid and 65 g. (0.2 mole) of quinine in dry acetone, and recrystallizing the resultant salt twice from dry acetone. The salt was hydrolyzed with dilute hydrochloric acid to give (−)-3,3-dimethylcyclohexanecarboxylic acid, b.p. 99.5–100° (0.12 mm.), $[\alpha]^{25}\mathrm{D}$ 1.14° (*l* 1 dm., neat). Reduction of 1 g. (0.0064 mole) of this active acid by the same procedure as in Part A gave 0.6 g. (66%) of (−)-3,3-dimethylcyclohexylcarbinol, b.p. 89° (10 mm.), $n^{25}\mathrm{D}$ 1.4600, $[\alpha]^{24}\mathrm{D}$ 2.07° (*l* 1 dm., neat).

Infrared Analysis.—Determinations of the isomeric composition of the mixtures of *cis*- and *trans*-3-methylcyclohexanecarboxylic acid from the Grignard reactions were carried out using a Baird Associates recording infrared spectrophotometer, model B. The spectra were taken of 5% solutions of the samples in carbon disulfide in 0.1 mm. sodium chloride cells. The percentage compositions were determined by comparison of the spectra of the samples with those of synthetic mixtures of the pure isomeric 3-methylcyclohexanecarboxylic acids using the absorbancies at 7.86 and 8.04 μ.

The amount of isomeric impurity in the 3-methylcyclohexyl chlorides was estimated by using absorbancies at 7.48 and 14.68 μ and assuming additive absorbancies at these wave lengths.[30] The samples were run as pure liquid films in 0.041-mm. sodium chloride cells.

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(30) E. I. Stearns in M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 369.

MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Kinetics of the Friedel–Crafts Benzoylation of Benzene with Aluminum Chloride as Catalyst and Benzoyl Chloride as Solvent[1,2]

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In benzoyl chloride as solvent, aluminum chloride brings about the quantitative benzoylation of benzene. The reaction exhibits simple second-order kinetics, first order in aluminum chloride and first order in benzene, with the second-order rate constant being essentially independent of the initial concentration of the reactants. On the assumption that the aluminum chloride exists in benzoyl chloride solution as the addition compound, $C_6H_5COCl{\cdot}AlCl_3$, the reaction proceeds in accordance with the equation 1 and the rate expression is given in equation 3. From the variation in the rate constant with temperature, $\Delta H^{\ddagger} = +15.1$ kcal./mole and $\Delta S^{\ddagger} = -27.2$ e.u. Substitution of a portion of the benzoyl chloride solvent by cyclohexane results in a decrease in the rate constant. Thus the observed relative rates are 1, $^1/_4$, $^1/_{13}$, $^1/_{22}$ in solvents containing 0, 25, 51 and 74% cyclohexane, respectively. Possible reaction mechanisms consistent with the observed kinetics are considered.

The Friedel–Crafts acylation reaction appeared to possess certain desirable features for our studies of the factors influencing the catalytic effectiveness of polyvalent metal halides and the effect of substituents on the rate of aromatic substitution. For these objectives we required a reaction with relatively simple kinetics.

The kinetics of the Friedel–Crafts acylation re-

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(1) The Catalytic Halides. XXI. Directive Effects in Aromatic Substitution. XXI.

(2) Based upon a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree.

(3) Research assistant on a project supported by the Atomic Energy Commission, 1953–1954; National Science Foundation Predoctoral Fellow, 1954–1955.