occurred and the solution turned a deep red in color; after standing for 10 minutes the solution was evaporated by means of compressed air. A dark-colored oil was obtained which changed into a solid, m.p. 145–150°, and weighed 382 mg. (87%). Four recrystallizations from anhydrous acetone gave a light gray material, m.p. 155–157°. A mixed melting point with an authentic sample[14] melted at 157–158° and infrared spectra of the two samples were identical.

1-(*m*-Chlorophenyl)-aziridine.—A mixture of 352 mg. of 1-(*m*-chlorophenyl)-Δ^2-1,2,3-triazoline and 75 ml. of heptane was refluxed 20 hours. The mixture was cooled and several pellets of sodium hydroxide added to prevent polymerization of the formed aziridine.[15] The heptane was evaporated until a volume of 9.5 ml. remained. An infrared spectrum of an authentic sample[15] of 1-(*m*-chlorophenyl)-aziridine dissolved in heptane was identical with a spectrum of the reaction mixture. All the heptane was then evaporated and the residual oil was removed from the pellets of sodium hydroxide. The crude 1-(*m*-chlorophenyl)-aziridine (210 mg.) had an infrared spectrum that identically corresponded in every respect to the spectrum of the true sample.

Acknowledgment.—The authors thank Miss Jo Ruff who checked the procedures for the preparation and isomerization of the 1-arylazoaziridines and Mr. William G. Kenyon who did the initial isomerizations on 1-*p*-nitrophenylazoaziridine.

[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS 10, O.]

Synthesis and Reactions of 4-Trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone[1]

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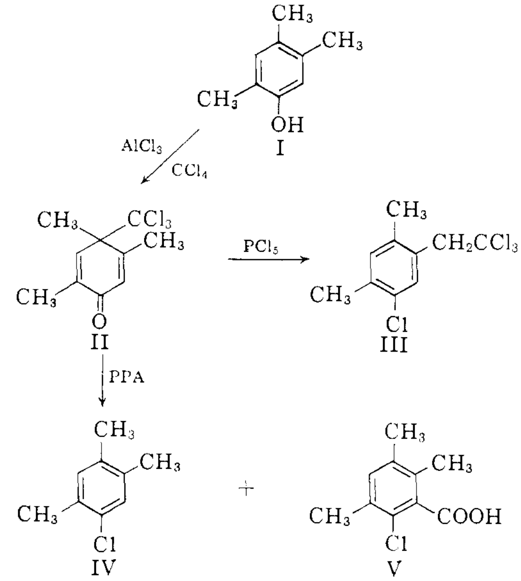
2,4,5-Trimethylphenol (I), aluminum chloride and carbon tetrachloride react to give 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (II) in 70% yield; II reacts with phosphorus pentachloride to yield 2,4-dimethyl-5-(β,β,β-trichloroethyl)-chlorobenzene (III) in 91% yield, and with polyphosphoric acid to yield 2,4,5-trimethylchlorobenzene (IV) (*ca.* 20%) and 2-chloro-3,5,6-trimethylbenzoic acid (V) (*ca.* 40%).

The reactions of *p*-cresol[3a,4] and 3,4-dimethylphenol[5] with carbon tetrachloride and aluminum chloride to form 4-methyl-4-trichloromethyl-2,5-cyclohexadienone and 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone, respectively, have been described. In view of the interesting reactions of these dienones with phosphorus pentachloride[5,6] and polyphosphoric acid[6] (PPA), we have extended our studies to 2,4,5-trimethylphenol (I).

On reaction in carbon tetrachloride solution with aluminum chloride, Compound I was converted smoothly into 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (II). The latter was converted into 2,4-dimethyl-5-(β,β,β-trichloroethyl)-chlorobenzene (III) by treatment with phosphorus pentachloride and into a mixture of 2,4,5-trimethylchlorobenzene (IV) and 2-chloro-3,5,6-trimethylbenzoic acid (V) by treatment with polyphosphoric acid. Thus, the chemistry of I and II is similar to that of their analogs.[5,6] The formation of products is satisfactorily explained by the mechanisms previously postulated.[5,6] Of interest is the relatively large yield of the acid V which results from the 1,3-migration of the trichloromethyl group to a position on the nucleus which has two *ortho* groups, methyl and chloro. In the case of the analogous rearrangement of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone with PPA, two acids were formed[6]; namely, 2-chloro-4,5-dimethylbenzoic acid (in the 50–60% yield range) and 2-chloro-5,6-dimethylbenzoic acid (in 3% yield). Since the formation of the latter acid involves migration to a position having two *ortho* substituents, it was of interest to see what would happen if there were only such a position open in the starting dienone. The results herein reported show that rearrangement of a trichloromethyl group to a hindered position on the ring occurs readily.



The structure of III was established as follows. Dehydrochlorination yielded 5-(β,β-dichlorovinyl)-2,4-dimethylchlorobenzene (VI) which was oxidized to 5-chloro-2,4-dimethylbenzoic acid (VIIa). As the latter was unknown, its structure was established by conversion into dimethyl 2,4-dimethyl-1,3-benzenedicarboxylate[7] (VIIIb).

The structure of IV was proved by oxidation of durene[8] by nitric acid[9] to an acid which must be

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[2] Postdoctoral fellow, 1958–1959.

[3] Postdoctoral fellow, 1960–1961.

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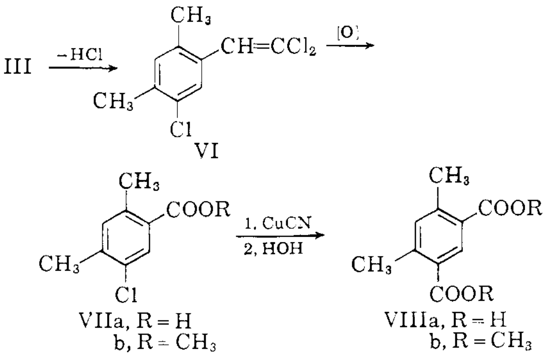

2,4,5-trimethylbenzoic acid. Degradation of this acid to the corresponding amine followed by replacement of the amino group by chlorine yielded 2,4,5-trimethylchlorobenzene which was shown to be identical to IV obtained from II.

The structure of V was established as follows. Degradation of V to the corresponding amine followed by deamination yielded IV. Reaction of the methyl ester of V with cuprous cyanide followed by hydrolysis yielded an acid which, as it readily formed an anhydride, must be 3,5,6-trimethylphthalic anhydride.

Experimental[10]

4-Trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (II).—A solution of 136 g. of 2,4,5-trimethylphenol[11] in 300 ml. of distilled carbon tetrachloride was added during 3 hr. to a stirred slurry of 266 g. of anhydrous aluminum chloride[12] in 300 ml. of carbon tetrachloride held at room temperature. After stirring for 2 hr. more the dark mixture was poured on ice and hydrochloric acid. The organic layer was washed with dilute acid and with 100 ml. of 20% sodium hydroxide. After removal of solvent the residue was distilled to yield 177 g. (70%) of II, b.p. 115–117° at *ca.* 1 mm. This material, which crystallized on standing, was suitable for further work. The analytical sample, obtained with little loss on crystallization from Skellysolve B (petroleum ether, b.p. 60–70°), melted at 74–75°.

Anal. Calcd. for $C_{10}H_{11}Cl_3O$: C, 47.4; H, 4.4; Cl, 42.0. Found: C, 47.5; H, 4.6; Cl, 42.0.

2,4-Dimethyl-5-(β,β,β-trichloroethyl)-chlorobenzene (III).—A solution of 25.3 g. of II in 20 ml. of methylene chloride was added slowly to a suspension of 20.8 g. of phosphorus pentachloride in 30 ml. of methylene chloride. After the reaction mixture had become a clear yellow solution it was held at reflux for 3 hr. The solvent and phosphorus oxychloride were removed under reduced pressure and the residue distilled to yield III as a slightly yellow oil, b.p. 105–106° at 1 mm., in 85% yield.

Anal. Calcd. for $C_{10}H_{10}Cl_4$: C, 44.2; H, 3.7; Cl, 52.1. Found: C, 44.3; H, 4.0; Cl, 51.9.

In a similar run in which the solvent was carbon tetrachloride, the yield was slightly better (91%).

Proof of Structure of III.—After refluxing a solution of 22.4 g. of III with 30 ml. of benzene containing 20 ml. of piperidine for 5 hr. and cooling, 9.2 g. (92%) of piperidine hydrochloride was collected by filtration. After the usual workup[10] there was obtained 18.1 g. (93%) of 5-(β,β-dichlorovinyl)-2,4-dimethylchlorobenzene, b.p. 93–96° at about 0.4 mm., $n^{21}\text{D}$ 1.580.

Anal. Calcd. for $C_{10}H_9Cl_3$: C, 51.0; H, 3.9; Cl, 45.2. Found: C, 51.0; H, 3.7; Cl, 45.1.

To a stirred solution of 10.4 g. of III in 60 ml. of acetone and 6 ml. of water was added 16 g. of powdered potassium permanganate during 1 hr. After 30 min., more aqueous oxalic acid was added to destroy the permanganate. The acid fraction of the oxidation products amounted to 5.4 g. (66%) of 5-chloro-2,4-dimethylbenzoic acid,[13] m.p. 164–165°, on crystallization from methanol.

Anal. Calcd. for $C_9H_9ClO_2$: C, 58.6; H, 4.9; Cl, 19.2. Found: C, 58.4; H, 5.1; Cl, 19.0.

On treatment of this acid with diazomethane, an almost quantitative yield of methyl 5-chloro-2,4-dimethylbenzoate m.p. 59–60°, was obtained on recrystallization from Skellysolve B.

Anal. Calcd. for $C_{10}H_{11}ClO_2$: C, 60.5; H, 5.6; Cl, 17.9. Found: C, 60.6; H, 5.7; Cl, 17.8.

The above ester (4.2 g.) was converted to the corresponding cyanoester by heating with cuprous cyanide (2.2 g.) in 15 ml. of N-methylpyrrolidone at 240–250° for 4 hr. as described.[14] The crude cyanoester was hydrolyzed by heating at reflux with aqueous potassium hydroxide for 2 hr. The mixture of acids obtained was dried and triturated twice with dry ether. The insoluble portion (0.7 g.), m.p. > 300°, was treated with diazomethane and the ester recrystallized from methanol to yield 360 mg. of pure dimethyl 4,6-dimethylisophthalate,[7] m.p. and mixed m.p. 75–76°. The other sample of this ester was prepared from 4,6-dibromo-*m*-xylene[15] *via* 4,6-dicyano-*m*-xylene,[16] using cuprous cyanide in N-methylpyrrolidone as described,[14] followed by hydrolysis to 4,6-dimethylisophthalic acid,[9] m.p. >300°, and treatment of the latter with diazomethane.

Reaction of II with PPA.—To 40 g. of warm PPA was added gradually 25.3 g. of powdered I, the temperature being raised to 90°. The mixture foamed and turned orange color and then red. The evolved gases were led through traps containing aniline in benzene. Aniline hydrochloride and carbanilide[17] were identified as the solid products. After 1 hr. the viscous red mixture was cooled and treated cautiously with 100 ml. of 20% sodium hydroxide. The organic products were taken into ether–benzene and treated as usual.[10] From the neutral fraction after distillation and crystallization from ethanol was obtained 4.9 g. (26%) of 2,4,5-trimethylchlorobenzene,[18] m.p. 72.5–73.5°. This compound did not depress the m.p. of a sample made from durene as described in the Discussion.

From the acid fraction 8.6 g. (45%) of an acid, m.p. 163–164°, shown (below) to be 2-chloro-3,5,6-trimethylbenzoic acid (V) was obtained on recrystallization from cyclohexane.

Anal. Calcd. for $C_{10}H_{11}ClO_2$: C, 60.5; H, 5.6; Cl, 17.9. Found: C, 60.4; H, 5.8; Cl, 17.7.

On decarboxylation of a small amount of V *via* the Schmidt[19] degradation to 2-chloro-3,5,6-trimethylaniline (not isolated) and deamination using hypophosphorus acid,[20] 2,4,5-trimethylchlorobenzene, m.p. 71–72°, was obtained. This m.p. was not depressed on mixing with an authentic sample of 72.5–73.5°.

The position of the carboxyl group in V was established as follows. A sample of V was converted to the methyl ester with diazomethane. On heating with cuprous cyanide in N-methylpyrrolidone[14] at reflux for 12 hr., there was obtained methyl 6-cyano-2,3,5-trimethylbenzoate, m.p. 67.5–69.0°.

Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.9; H, 6.5. Found: C, 70.7; H, 6.5.

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(10) All melting points and boiling points are uncorrected. The phrase "worked up in the usual way" means that an ether–benzene (1:1) layer of the organic products was washed successively with dilute hydrochloric acid, dilute sodium carbonate solution and saturated sodium chloride solution, followed by filtration through a small bed of anhydrous magnesium sulfate. The solvent was then removed by distillation at atmospheric pressure or under vacuum. All microanalyses were by the Galbraith Laboratories, Knoxville, Tenn.

(11) Used as obtained from the Aldrich Chemical Co., Milwaukee, Wis.

(12) Sublimed technical grade, Ohio–Apex Division, Food Machinery and Chemical Corp.

(13) G. T. Morgan and W. J. Hickinbottom, *J. Chem. Soc.*, 1891 (1921), reported a m.p. of 165–165° for this acid, but did not establish the structure.

(14) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961).

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(16) H. Diesbach, *Helv. Chim. Acta*, **6**, 541 (1923).

(17) A. W. Hofmann, *Ann.*, **70**, 140 (1849), prepared carbanilide by passing phosgene into aniline.

(18) G. Schultz, *Ber.*, **42**, 3604 (1909), reported a m.p. of 70–71°.

(19) H. Wolff in "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 327.

(20) N. Kornblum, *ibid.*, Vol. II, 1944, p. 277.

On hydrolysis by heating 1.25 g. of this ester in 5 ml. of acetic acid and 10 ml. of 85% sulfuric acid on the steam-bath for 6 hr., there was obtained 3,4,6-trimethylphthalic anhydride, m.p. 123–124°, on crystallization from Skellysolve B. The formation of anhydride locates the original carboxyl group *ortho* to the chlorine.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3. Found: C, 69.4; H, 5.3.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF FLORIDA, GAINESVILLE, FLA.]

The Stereochemistry and Reaction Path of Borohydride Reductions of 4-*t*-Butylcyclohexanone in Diglyme[1]

BY W. M. JONES AND HUGH E. WISE, JR.

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The stereochemistry of the reduction of 4-*t*-butylcyclohexanone with a variety of borohydrides has been examined. All reductions were effected in the same solvent (diglyme) and at the same temperature (20°). In an attempt to gain some information regarding the stereochemistry of the first step of the borohydride reductions, the reactions were studied in the presence of triethylamine, a reagent which stops the reductions after the first hydride has been used. That the reductions in the presence of the amine actually gave some indication of the stereochemistry of the first step in a normal borohydride reduction was demonstrated by examining the stereochemistry of the reduction of the ketone with diborane in the presence of the sodium salt of 4-*t*-butylcyclohexanol. The fact that the first step in the reduction led to less of the *axial* (*cis*) alcohol than the average of all four steps is interpreted as indicating that at least one of the last three steps in the reduction must involve alkoxy borohydride. It was also found that, in diglyme, the lithium cation affects the stereochemistry of the reduction.

Although the stereochemistry of the reduction of alicyclic and polycyclic ketones with various borohydrides has been rather thoroughly investigated,[2-6] interpretation of the results has invariably been confused by the fact that the stereochemistry of the first step which is generally agreed to involve the borohydride ion[7-10] could not be isolated from the last three steps. In fact, although Brown and his co-workers[9,10] have specifically stated that the last three steps in borohydride reductions involve the alkoxy borohydrides, the fact that it has been previously found[11,12] that diborane effects very rapid reduction of a ketone suggested to us the possibility that one, two or all three of the last three steps of the borohydride reduction could conceivably involve borine (or diborane) and its alkoxy derivatives.

$$R_2CO + BH_4^- \longrightarrow H_3BOCHR_2^-$$

$$R_2CO + H_3BOCHR_2^- \longrightarrow H_2B(OCHR_2)_2^-$$

$$R_2CO + H_2B(OCHR_2)_2^- \longrightarrow HB(OCHR_2)_3^-$$

$$R_2CO + HB(OCHR_2)_3^- \longrightarrow B(OCHR_2)_4^-$$

$$R_2CO + BH_4^- \longrightarrow R_2CHO^- + BH_3$$

$$R_2CO + BH_3 \longrightarrow R_2CHOBH_2$$

$$R_2CO + R_2CHOBH_2 \longrightarrow (R_2CHO)_2BH$$

$$R_2CO + (R_2CHO)_2BH \longrightarrow (R_2CHO)_3B$$

Considering this possibility, the nature of the problem of assigning the steric requirements of the borohydride ion from studies of the stereochemistry of borohydride reductions can best be presented in the way of an example. The reduction of 4-*t*-butylcyclohexanone with sodium borohydride in diglyme (diethylene glycol dimethyl ether) has been found (see Discussion) to give 21% of the thermodynamically less stable (*axial*) alcohol. If the last three steps in the reduction actually involved only the borines, then, in view of the fact that the reduction with the borines has been found to give only 12.6% of the *axial* isomer (see Discussion), the first step of the reduction would require in the range of 40–50% of the *axial* isomer. If, on the other hand, the last three steps involve only the alkoxy borohydrides, then it follows from the observation that alkoxy borohydrides give more of the *axial* alcohol than the total reduction (see Discussion), and that the first step of the reduction should give less than 20% of the *axial* alcohol. Thus, arguments about the steric requirements of the borohydride ion based solely on averages of the stereochemistry of four reduction steps in which the borohydride ion is the participating species in only one of these steps obviously leave something to be desired.

In the course of our reading, an observation by Brown, Mead and Subba Rao[10] suggested a possible method for obviating this problem. Thus, whereas borohydride reductions generally involve a slow first step followed by three rapid reactions.[8-10] Brown and co-workers found that, in the presence of triethylamine, the reduction stopped after the first step. Although we have found that the reason which was given for this phenomenon was incor-

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[1] Based upon a theses submitted by H. E. Wise, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] For by far the most comprehensive study and the best available discussion on this subject, see A. H. Beckett, N. J. Harper, A. D. Balton and T. H. E. Watts, *Tetrahedron*, **6**, 319 (1959).

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