chlorobenzene, m.p. and mixed m.p. with authentic compound,[24] 69.5–71.0°.

b. Since the acid VI was hindered,[25] the structure 2-chloro-5,6-dimethylbenzoic acid was indicated. This was proved by replacement of the carboxyl by amino, essentially as described above[22] and deamination, also as above,[23] to yield 3,4-dimethylchlorobenzene which was oxidized to 4-chlorophthalic acid.[26]

**Treatment of I with PPA.**[10]—A mixture of 23.6 g. of I and 77 g. of PPA was stirred at 90–100° for 5 hours, during which a stream of dry nitrogen carried all gases formed into a trap containing aniline in benzene. The cooled reaction mixture was extracted several times with ether. After removal of the ether the remaining oil was treated with cold concentrated ammonium hydroxide. This mixture, containing white solid, was extracted with Skellysolve B. From these extracts 1.13 g. (9%) of *p*-chlorotoluene, b.p. 159–163°, was obtained. The infrared spectrum was identical to that obtained from pure *p*-chlorotoluene.

The above white solid yielded 3.8 g. (22.5%) of 4-chloro-2-methylbenzamide, m.p. 167.5–170.0°.

After extraction with ether, the above PPA solution was diluted with 500 ml. of water, and extracted three times with 75-ml. portions of 1:1 ether–benzene. On extraction of these extracts with alkali, acidification of these extracts with acid, and crystallization from benzene there was obtained 8.4 g. (49%) of 4-chloro-2-methylbenzoic acid (VIII), m.p. 168.5–170.0°. This acid[27] proved identical to that obtained on hydrolysis of 4-chloro-2-methylbenzotrichloride, itself obtained by treatment of I with phosphorus pentachloride[6] (equation 1).

Thus the total quantity of acid VIII produced was about 71.5% along with 9% of *p*-chlorotoluene (IX). When excess hydrogen chloride was added to the PPA before adding I, the quantity of VIII rose to about 82% while the amount of IX formed fell to about 5% (average of two runs in which the procedure was essentially unchanged from that described above).

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(24) L. I. Smith and C. L. Moyle, THIS JOURNAL, **58**, 1 (1936), prepared 2,4,5-trimethylchlorobenzene, m.p. 70.5–71.0°, by chlorination of 1,2,4-trimethylbenzene. Our authentic sample, m.p. 70.0–71.0°, was prepared by this method.

(25) Further evidence for this, in addition to the failure of esterification by Fischer–Speier method, lies in the fact that when a solution of VI in 100% sulfuric acid was poured into methanol, the methyl ester was formed; see M. S. Newman, *ibid.*, **63**, 2431 (1941). When acid V was so treated it was recovered unchanged.

(26) We are indebted to Mr. John Eberwein for this conversion. The 4-chlorophthalic acid was further converted to 4-chlorophthalic anhydride, m.p. and mixed m.p. with an authentic sample, m.p. 96–98°.

(27) The structure proof of this acid as 4-chloro-2-methylbenzoic acid follows from the fact that the structure of this isomeric 5-chloro-2-methylbenzoic acid has been established (see above, part f) and that both acids yield 4-chlorophthalic acid on oxidation.

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

# Rearrangement of 4-Methyl-4-trichloromethyl-2,5-cyclohexadienols[1,2]

BY MELVIN S. NEWMAN, JOHN EBERWEIN AND LOUIS L. WOOD, JR.

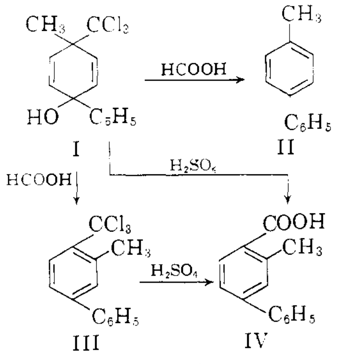
RECEIVED MAY 11, 1959

It is shown that in two cases in which a trichloromethyl group was reported to undergo a 1:2-shift, errors in identification of products were made. 4-Methyl-1-phenyl-4-trichloromethyl-2,5-cyclohexadienol (I) yields 4 methylbiphenyl (II) on treatment with cold formic acid, and 2,6-dichloro-4-methyl-4-trichloromethyl-2,5-cyclohexadienol (VIII), yields 3,5-dichloro-2-methylbenzoic acid (X) on treatment with a solution of sulfuric acid in acetic acid at reflux.

4 - Methyl - 4 - trichloromethyl - 2,5 - cyclohexadienols undergo a variety of rearrangements on heating or treatment with acids.[3–5] Most of the examples involve either a 1:2-shift of the methyl group or a 1:3- or 1:5-shift of the trichloromethyl group. However, there are two cases in which a 1:2-shift of the trichloromethyl group has been claimed.[3,6] In this paper we show that errors in identification of products have been made in these two cases.

The first case involves the reported[3] rearrangement of 4-methyl-1-phenyl-4-trichloromethylcyclohexadienol (I) to *p*-ethylbiphenyl on treatment with formic acid in the cold. The ethyl group was presumably formed by reduction of a β,β,β-trichloroethyl group formed by a 1:2-shift of a trichloromethyl group. This result has previously been questioned[7] because the rearrangement product of I melted at 46–47°, whereas the melting points of *p*-methylbiphenyl (II) and of *p*-ethylbiphenyl are 47–48° and 34.0–34.5°, respectively.

We have repeated the preparation and rearrangement of I in formic acid and have proved that the hydrocarbon rearrangement product is *p*-methylbiphenyl (II). In addition to II (formed in about 25% yield) there were also obtained 3-methyl-4-trichloromethylbiphenyl (III) and 2-methyl-4-phenylbenzoic acid (IV) a product derivable from III on acidic hydrolysis.[3]



The starting compound I is prepared by reaction of phenylmagnesium bromide with 4-methyl-4-trichloromethyl-2,5-cyclohexadienone. A careful search for stereoisomers of I was made, but only one isomer was found. Even the crude carbinol frac-

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(1) Taken in part from the Ph.D. Thesis of L. L. Wood, Ohio State University, 1959.

(2) This research was supported in part by the United States Air Force under contract No. AF49(638)-277 monitored by the AF Office of Scientific Research of the Air Research and Development Command.

(3) K. von Auwers and W. Jülicher, *Ber.*, **55**, 2167 (1922).

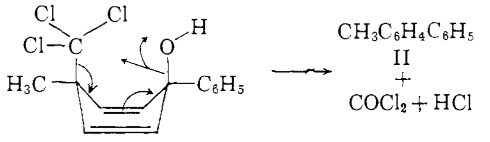
(4) R. L. Tse and M. S. Newman, *J. Org. Chem.*, **21**, 638 (1956).

(5) M. S. Newman and L. L. Wood, Jr., THIS JOURNAL, **81**, 6450 (1959).

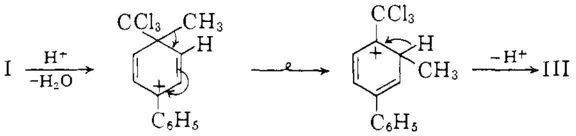
(6) H. Plieninger and G. Keilich, *Ber.*, **91**, 1893 (1958).

(7) W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, THIS JOURNAL, **68**, 1109 (1946).

tion had a narrow melting range. We do not know the stere chemistry of I but suggest that the trichloromethyl and hydroxyl groups are *cis*, not only because this geometry would be expected because of the directive influence of the bulky trichloromethyl group in the starting dienone, but also because of possible interaction leading to ready loss of these groups from I under the mild reaction conditions needed to form II. A study of molecular models shows that this interpretation is permissible.



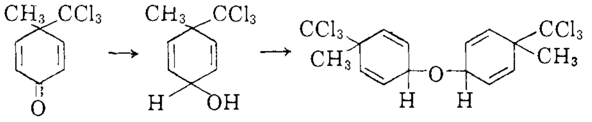
Interestingly, in other cases in which a trichloromethyl group is lost from the molecule[8] the proposed mechanism involves a 1:4 interaction (six atom cyclic mechanism) and formation of phosgene. In the above description of the reaction there is no function for the formic acid. There must be one since in acetic acid no reaction occurs without added sulfuric acid and the compound I is stable up to its melting point in the solid state. Possibly the formic acid esterifies the hydroxyl group before the intramolecular decomposition occurs. It seems certain that the acidity of formic acid is not directly involved in the formation of II since in the presence of strong acid[9] the products are III and IV



rather than II. Obviously further work must be carried out before the mechanism of the conversion of I to II is understood.

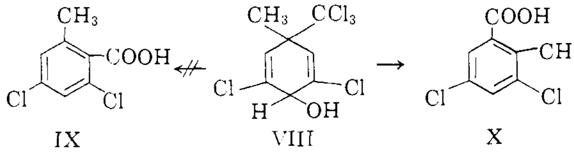
If *p*-ethylbiphenyl had been the true product, it would have arisen by reduction of a $\beta,\beta,\beta$-trichloroethyl group formed by a 1:2 shift of the trichloromethyl group to the 4-methyl group in I. That reduction to an ethyl group or degradation to a methyl group does not occur under the reaction conditions was proved by the fact that 4-methyl-3-($\beta,\beta,\beta$-trichloroethyl)-chlorobenzene[5] was stable to cold and even boiling formic acid.

In connection with attempts to isolate a stereoisomer of I, 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (V) was reduced with lithium aluminum hydride and by the Meerwein–Ponndorf–Verley method.[10] In each case high yields of 4-methyl-4-trichloromethyl-2,5-cyclohexadienol (VI), m.p. 136.5–137.5°, were obtained but we were unable to isolate a stereoisomer. However, on standing in an impure state, or on chromatography over silicic acid–silica, a substance was obtained which we believe to be di-(4-methyl-4-trichloromethyl-2,5-cyclohexadienyl) ether (VII) since, on treatment with sulfuric acid, it gave *o*-toluic acid in quantitative yield, as did VI.[3]



V VI VII

The second case in which the 1:2-shift of a trichloromethyl group was reported[6] involves the rearrangement of 2,6-dichloro-4-methyl-4-trichloromethyl-2,5-cyclohexadienol (VIII) into 2,4-dichloro-6-methylbenzoic acid (IX) on treatment with sulfuric acid in acetic acid at reflux. We have repeated this reaction and have proved that the rearranged product is 3,5-dichloro-2-methylbenzoic acid X.



IX VIII X

The rearranged acid was proved to have the structure X as follows. The carboxyl group was removed by a Schmidt reaction[11] followed by reductive deamination[12] to yield a dichlorotoluene. This was oxidized to an acid which proved to be 2,4-dichlorobenzoic acid. This result proves that the methyl group in VIII has made a 1:2-shift. It does not prove that the carboxyl group in the acid in question is as shown in formula X, but we regard it as extremely unlikely that the rearranged acid in question is either 2,4-dichloro-5-methylbenzoic acid or 2,6-dichloro-3-methylbenzoic acid. Although these would yield 2,4-dichlorobenzoic acid on treatment as described above, the formulation of the acid in question as either of these acids is contraindicated since in all known cases of acid-catalyzed rearrangement of 4-methyl-4-trichloromethyl-2,5-cyclohexadienols, the methyl or the trichloromethyl group migrates, but not both (unless the trichloromethyl group is lost altogether, as shown in the first example in this paper).

The fact that the rearranged acid is readily esterified by refluxing in acidified methanol rules out the structure IX originally proposed[6] and also that of 2,6-dichloro-3-methylbenzoic acid since these sterically hindered acids would not esterify under these conditions.[13]

To summarize, it may be stated that in all known rearrangements of 4-methyl-4-trichloromethyl-2,5-cyclohexadienols and 4-methyl-4-trichloromethyl-2,5-cyclohexadienones, if the methyl group migrates, it does so by a 1:2-shift whereas if the trichloromethyl group migrates, it does so by a 1:3- or a 1:5-shift. No exceptions to these rules are known.

## Experimental[14]

**4-Methyl-1-phenyl-4-trichloromethyl-2,5-cyclohexadienol (I).**—A solution of 42.1 g. of 4-methyl-4-trichloromethyl-

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[8] Compare the conversions of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone to *p*-chlorotoluene and of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone to 3,4-dimethylchlorobenzene on treatment with polyphosphoric acid; see ref. 5.

[9] The mechanism for the formation of III from I on treatment with acid undoubtedly involves formation of a carbonium ion which is stabilized by a 1:2-shift of a methyl group followed by loss of a proton.

[10] A. L. Wilds, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 178.

[11] Carried out as described in H. Wolff, *ibid.*, Vol. III, 1946, p. 327.

[12] According to N. Kornblum, *ibid.*, Vol. II, 1945, p. 262.

[13] Note that 2-chloro-5,6-dimethylbenzoic acid (VI) in ref. 5 is not esterified under these conditions.

[14] All melting points are corrected. All analyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

2,5-cyclohexadienone[15] in 250 ml. of dry ether was added during 15 minutes to a stirred excess of phenylmagnesium bromide in ether. The mixture was refluxed for 45 minutes and then worked up in a conventional way to yield 47.0 g. (86%) of crude I, m.p. 116–120°. Recrystallization from benzene yielded 45.8 g. of colorless I, m.p.[16] 120.0–121.0°. Attempts to isolate another solid from the remaining reaction products were in vain.

**Reaction of I with Formic Acid.**—A mixture of 29.9 g. of I and 300 ml. of 90% formic acid was stirred at 0–5° for 8 hours. During this time the solid particles of I gradually disappeared and a pale yellow oil was formed. The reaction mixture was poured on 1 kg. of ice and this mixture extracted thrice with ether. The ethereal extract, after washing with 10% aqueous potassium hydroxide solution (extracts saved, see below), water, and saturated sodium chloride solution, was dried over anhydrous magnesium sulfate. Removal of the ether left 15.5 g. of a yellow oil which on distillation was separated into 4.4 g. of a fraction, b.p. 100–130° at 5 mm., which partly solidified, and 3.7 g. of a fraction, b.p. 150–190° at 5 mm. At this point, distillation was stopped as the residue was decomposing with the evolution of hydrogen chloride. Recrystallization of the lower boiling fraction from alcohol afforded 4.3 g. (25%) of *p*-methylbiphenyl (II), m.p. 45.5–47.0°, undepressed by mixing with an authentic sample of *p*-methylbiphenyl, m.p. 46.5–47.0°, prepared as described below. The infrared spectra of the two substances were identical.

From the above higher boiling fraction, a small amount of a solid, m.p. 88.5–90.0°, was obtained. Since this solid, on hydrolysis in concentrated sulfuric acid, yielded 2-methyl-4-phenylbenzoic acid[3] (IV), m.p. 169.0–171.0°, it was undoubtedly 3-methyl-4-trichloromethylbiphenyl (III).

*Anal.* Calcd. for $C_{14}H_{11}Cl_3$: C, 58.9; H, 3.9; Cl, 37.3. Found: C, 59.0; H, 4.0; Cl, 36.9.

From the aqueous potassium hydroxide solutions mentioned above was obtained 6.4 g. (30%) of IV on acidification. This had undoubtedly come from hydrolysis of II in the 90% formic acid solvent. To check this, a sample of benzotrichloride was stirred in 90% formic acid for 12 hours at 20–25°. An almost quantitative yield of benzoic acid was obtained.

***p*-Methylbiphenyl (II).**—Reduction of 38.7 g. of *p*-phenylbenzoic acid, m.p. 223–225°, in 500 ml. of ether by addition to a stirred solution of 7.5 g. of lithium aluminum hydride in 300 ml. of ether during 1 hour afforded *p*-phenylbenzyl alcohol,[17] b.p. 170–175° at 8 mm., m.p. 105.0–107.0°, in 90% yield.

A mixture of 18.4 g. of *p*-phenylbenzyl alcohol, 0.6 g. of palladium chloride, 3.0 g. of activated charcoal (Darco G-60) and 75 ml. of alcohol was shaken under 50 p.s.i. of hydrogen. After 1 hour the theoretical amount of hydrogen had been absorbed and a conventional work-up afforded 14.0 g. (84%) of *p*-methylbiphenyl. A recrystallized and sublimed sample melted at 46.5–47.0°.

*p*-Ethylbiphenyl, m.p. 36–37°, prepared by a Clemmensen reduction of *p*-phenylacetophenone,[18] m.p. 118–120°, had an infrared spectrum which differed significantly from that of II, whereas the infrared absorption spectra of 4-methylbiphenyl was identical to that of II.

**2,6-Dichloro-4-methyl-4-trichloromethyl-2,5-cyclohexadienol (VIII).**—Reduction of 2,6-dichloro-4-methyl-4-trichloromethyl-2,5-cyclohexadienone by treatment with sodium borohydride as described[6] yielded VIII, m.p. 125.5–127.5°, in 74% yield.

**Rearrangement of VIII.**—A solution of 2.2 g. of VIII in 30 ml. of acetic acid and 15 ml. of concentrated sulfuric acid[19] was heated on a steam-bath for 2 hours. The mixture was diluted with water and the solid collected. Recrystallization from Skellysolve B (petroleum ether, b.p. 65–70°) yielded 1.0 g. of an acid, m.p. 183.5–184.5°. On refluxing with methanolic sulfuric acid, this acid was converted in high yield into the corresponding methyl ester, m.p. 45.5–46.5°, after recrystallization from Skellysolve B and sublimation.

*Anal.* Calcd. for $C_9H_8O_2Cl_2$: C, 49.6; H, 3.7. Found: C, 49.4; H, 3.7.

The above acid was shown to be 3,5-dichloro-2-methylbenzoic acid (X) as follows.

**Proof of Structure of X.**—The above acid (0.52 g.) was dissolved in 5 ml. of concentrated sulfuric acid and the solution was treated with several portions of sodium azide at 40° during two hours.[20] Dilution with water yielded an amine sulfate which was converted to the free amine by alkali. This amine was reductively deaminated[21] to a dichlorotoluene, which, on oxidation by refluxing with an excess of dilute potassium permanganate for 15 hours yielded 0.11 g. of an acid, after the customary workup and recrystallization from benzene–Skellysolve B, which melted at 161.0–162.0°, alone and mixed with an authentic sample of 2,4-dichlorobenzoic acid,[22] m.p. 161.0–162.0°.

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[15] Prepared as described in M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954).

[16] In ref. 3, a m.p. of 120.8–121.0° is given.

[17] J. von Braun, *Ann.*, **436**, 299 (1924).

[18] In ref. 7, a m.p. of 120.0–121.0° was reported.

[19] In ref. 6, a solution of 15 ml. of 20% sulfuric acid in 50 ml. of acetic acid was used. When we repeated this, no rearranged acid was obtained.

[20] See H. Wolff, ref. 11.

[21] According to N. Kornblum, ref. 12.

[22] M. Gomberg and L. H. Cone, *Ann.*, **370**, 183 (1909), give a m.p. of 164°. Our authentic sample was prepared by the oxidation of 2,4-dichlorobenzyl chloride.

COLUMBUS 10, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

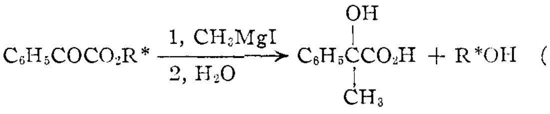
# Asymmetric Induction Studies with Optically Active Biphenyls. V. On the Unreliability of Absolute Configurational Assignments Based on Hydride Reductions of Phenylglyoxylates[1]

BY JEROME A. BERSON AND MICHAEL A. GREENBAUM

RECEIVED MAY 16, 1959

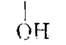
Reduction of phenyldihydrothebaine phenylglyoxylate with lithium aluminum hydride produces phenylethylene glycol with an absolute configuration enantiomeric with that of the atrolactic acid produced by addition of methylmagnesium iodide to the phenylglyoxylate. An abnormal reactivity order of the carbonyl groups of ethyl phenylglyoxylate is observed, the *ester* carbonyl group being reduced *faster* than the keto carbonyl group with sodium borohydride. This result demonstrates the need for extreme caution in assignments of absolute configuration based on hydride reductions of phenylglyoxylates.

Prelog's elegant "atrolactic acid method" of establishing absolute configurations of optically active alcohols[2] involves the reaction of methylmagnesium iodide with an optically active phenylglyoxylate, followed by saponification (1). In a



$$C_6H_5COCO_2R^* \xrightarrow[2,\ H_2O]{1,\ CH_3MgI} C_6H_5C(OH)(CH_3)CO_2H + R^*OH \quad (1)$$

formally analogous reaction (2), reduction of an



$$C_6H_5COCO_2R^* \xrightarrow{LiAlH_4} C_6H_5CH(OH)CH_2OH + R^*OH \quad (2)$$

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[1] This work was supported in part by a grant, NSF-G 4375, from the National Science Foundation.

[2] V. Prelog, *Bull. soc. chim. France*, 987 (1956), and references therein cited.