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

Reactions of 2,5-Cyclohexadienones Containing the Trichloromethyl Group[1,2]

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

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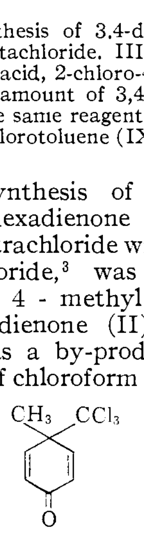
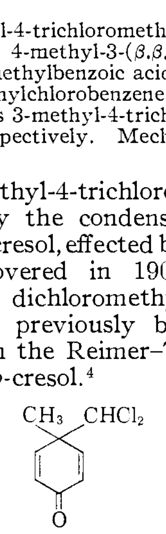
The synthesis of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (III) is described. On treatment with phosphorus pentachloride, III yields 4-methyl-3-(β,β,β-trichloroethyl)-chlorobenzene (IV). On treatment of III with polyphosphoric acid, 2-chloro-4,5-dimethylbenzoic acid (V) and 2-chloro-5,6-dimethylbenzoic acid (VI) are formed in addition to a small amount of 3,4-dimethylchlorobenzene (VII). Treatment of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (I) with the same reagents yields 3-methyl-4-trichloromethylchlorobenzene and 4-chloro-2-methylbenzoic acid (VII) (plus a little p-chlorotoluene (IX)), respectively. Mechanisms are proposed to account for these facts.

The synthesis of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (I) by the condensation of carbon tetrachloride with p-cresol, effected by aluminum chloride,[3] was discovered in 1906. The analogous 4 - methyl - 4 - dichloromethyl - 2,5-cyclohexadienone (II) had previously been discovered as a by-product in the Reimer–Tiemann reaction of chloroform with p-cresol.[4]



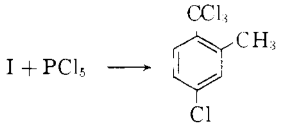
I



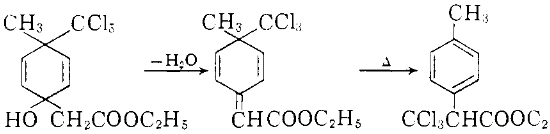
II

The chemistry of II and similar abnormal Reimer–Tiemann products has been studied extensively,[5] but only one study of the chemistry of I has appeared from that laboratory.[6]

The reactions of I and II and of products derived from them are remarkably similar. As far as molecular rearrangements are concerned, two types have been noted.[7] In one, the 4-methyl group rearranges to an adjacent position (a 1:2 shift, *e.g.*, eq. 1) and in the other, a 1:5 migration of the trichloromethyl group (or a dichloromethyl group) occurs[6,8] (eq. 2)

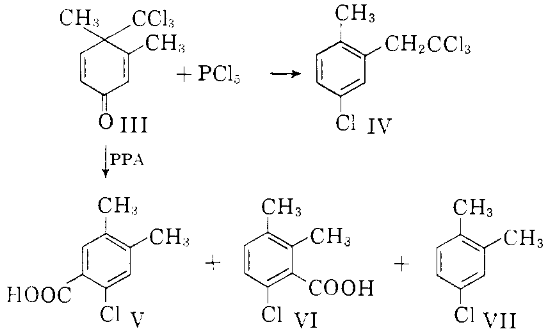


(1)



(2)

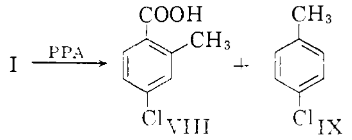
In this paper the synthesis of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (III) from 3,4-dimethylphenol and carbon tetrachloride is described as well as two new rearrangements involving 1:3 shifts of the trichloromethyl group. In one, treatment of III with phosphorus pentachloride yields 4-methyl-3-(β,β,β-trichloroethyl)-chlorobenzene[9] (IV) (eq. 3), and in the other (eq. 4), treatment of III with polyphosphoric acid[10] yields 2-chloro-4,5-dimethylbenzoic acid (V) and a small amount of 2-chloro-5,6-dimethylbenzoic acid (VI). The acids V and VI arise from the hydrolysis of the corresponding benzotrichlorides, the primary rearrangement products, as under similar conditions benzotrichloride is hydrolyzed to a mixture of benzoyl chloride and benzoic acid. In addition to the acids V and VI obtained in part as their acid chlorides, significant amounts of 3,4-dimethylchlorobenzene (VII) are obtained in the reaction of III with polyphosphoric acid.



(3)

(4)

Because of the unexpected results obtained in treating III with polyphosphoric acid, the behavior of I with this reagent was also examined. In this case the products were 2-methyl-4-chlorobenzoic acid (VIII) and p-chlorotoluene (IX).



(5)

The result summarized in equation 3 is discussed in a paper concerned with the mechanism of reaction of phosphorus pentachloride with ketones.[11] The reactions of I and III to give the products shown in equations 4 and 5 are unusual in that

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[1] This work formed part of the Ph.D. thesis of L. L. Wood, Jr., Ohio State University, 1959.

[2] This research was supported in part by the United States Air Force under contract No. AF 49(638)-277 monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.

[3] Th. Zinke and R. Suhl, *Ber.*, **39**, 4152 (1906).

[4] K. Auwers, *ibid.*, **17**, 2976 (1884).

[5] For example, K. Auwers, *ibid.*, **44**, 588, 788, 1595 (1911); K. Auwers and K. Ziegler, *Ann.*, **425**, 217, 280 (1921), and references therein.

[6] K. Auwers and W. Julicher, *Ber.*, **55**, 2167 (1922).

[7] See the accompanying paper, M. S. Newman, John Eberwein and L. L. Wood, Jr., THIS JOURNAL, **81**, 6454 (1959), for correction of errors which supposedly describe other types of rearrangement.

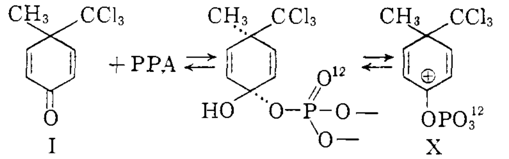
[8] For additional examples of this type see R. L. Tse and M. S. Newman, *J. Org. Chem.*, **21**, 638 (1956).

[9] M. S. Newman and L. L. Wood, *ibid.*, **23**, 1236 (1958).

[10] A mixture of phosphoric acid and phosphorus pentoxide, hereinafter referred to as PPA; see R. Bell, *Ind. Eng. Chem.*, **40**, 1464 (1948). We wish to thank the Victor Chemical Co. for a generous gift of polyphosphoric acid.

[11] M. S. Newman and L. L. Wood, THIS JOURNAL, **81**, 4300 (1959).

the only source of the nuclear chlorine atoms is the trichloromethyl group. In order to account for the results, we propose the following schemes as working hypotheses.



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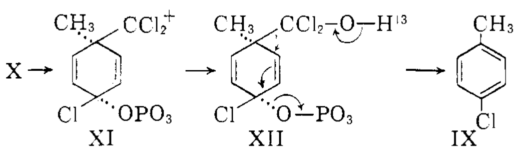

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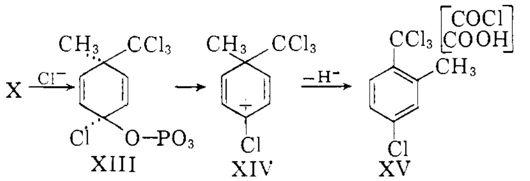


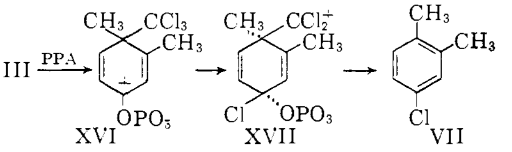
(8)

The key intermediate in the reactions between I and PPA is the carbonium ion X. Before any significant quantity of hydrogen chloride is produced by following reactions, the ion X has no external source of chloride ions. Hence an intramolecular transfer of chloride ion occurs to yield XI.[14] This is speedily acted on by any oxygenated species (shown in equation 7 as OH, but in reality it might be an oxygen–phosphorus bond) to yield a cyclohexadiene intermediate XII which then decomposes as shown to yield *p*-chlorotoluene and phosgene in addition to a phosphoric acid species. The phosgene formed is partly hydrolyzed to carbon dioxide and hydrogen chloride and partly volatilized (see Experimental).

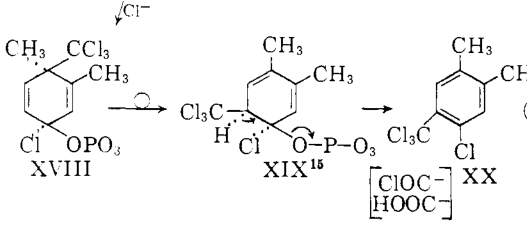
As soon as the availability of chloride ions (from formation of hydrogen chloride) increases, X reacts to yield the intermediate XIII which then loses the polyphosphoric acid moiety to yield the chlorocarbonium ion XIV. The latter then undergoes a Wagner–Meerwein type 1,2-shift of a methyl group, followed by loss of a proton to yield 4-chloro-2-methylbenzotrichloride (XV) which, in the polyphosphoric acid medium, is converted partly to the corresponding acid chloride and acid VIII (see Experimental).

The validity of the above mechanism is supported by the experimental observation that if the polyphosphoric acid is saturated with hydrogen chloride before reaction with I, the proportion of *p*-chlorotoluene produced decreases from about 9 to 5% whereas the amount of 4-chloro-2-methylbenzoic acid (VIII) is increased from about 72 to about 82%. However, since some *p*-chlorotoluene is still produced under these conditions (see Experimental) there must be a significant tendency for intramolecular transfer of a chloride ion in X to form XI.

The reaction products from III and polyphosphoric acid are explained by similar processes. The presence of the additional methyl group introduces a steric factor which affects the type of products formed.



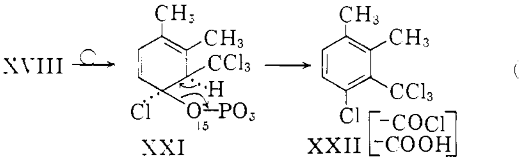
(9)



(10)

The reaction of III with polyphosphoric acid is similar to that of I and yields the carbonium ion XVI, which, on internal transfer of a chloride ion from the trichloromethyl group, yields XVII, and eventually, 3,4-dimethylchlorobenzene (VII).

The reaction of XVI with chloride ion produces the cyclohexadiene intermediate XVIII which differs from the similar intermediate XIII only by the extra methyl group. However, this methyl group exerts a steric effect because of the crowding it produces. Because of this steric effect, the tendency of the trichloromethyl group to migrate is increased, with the result that the rearranged intermediate XIX is formed. Elimination (*trans*[15]) of polyphosphoric acid from XIX produces XX, which, under the influence of the medium, is converted into a mixture of the corresponding acid chloride and acid V. The formation of the acid VI from XVIII may be pictured by an analogous route *via* XXI and XXII (equation 11). The fact that the trichloromethyl group makes a 1:3-shift to a more hindered position explains the small quantity (*ca.* 3%) of this isomer produced.



(11)

As in the case of the reaction of I with PPA,[10] the addition of hydrogen chloride to the PPA cuts down the quantity of 3,4-dimethylchlorobenzene (VII) formed from about 19 to about 13%, while the yield of acids V and VI is increased from about 56 to about 67%. Here again there appears to be a significant tendency to intramolecular transfer of a chloride ion.

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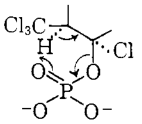
[12] The OPO_3 fragment represents the polyphosphoric acid[10] moiety of indefinite composition and not a doubly negatively charged anion.

[13] The addition of OH is shown, but any O–P (phosphorus-containing) moiety could be substituted. The main function of the medium here is to provide an oxygen which eventually leads to the formation of phosgene (later carbon dioxide).

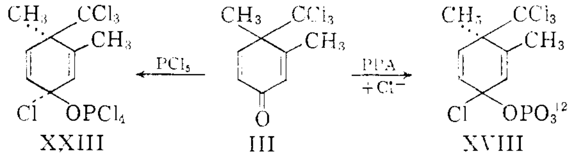
[14] The probable stereochemistry of XI is shown here as well as in other cases where stereoisomers might be involved. It is assumed that the bulk of the CCl_3 group is the determining factor when an external reagent reacts with a carbonium ion, *e.g.*, equation 8.

[15] The elimination of phosphoric acid from XIX and XXI may occur by a six atom cyclic mechanism in which the hydrogen becomes attached to a doubly bonded oxygen atom in the PO_3 grouping, *e.g.*, i.

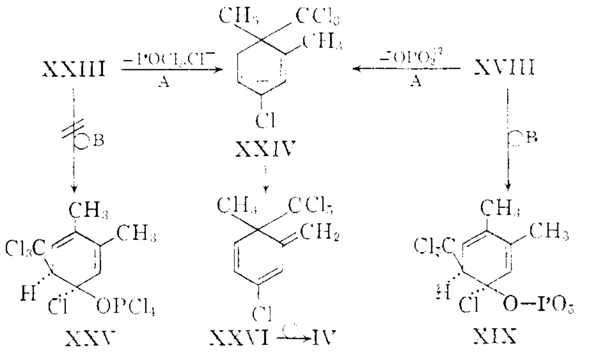


The significant feature of the chemistry of III above outlined is that two new 1:3-rearrangements of the trichloromethyl group have been discovered: a shift to an adjacent methyl group attached to the ring (in equation 3); and shifts to a *m*-position of the ring (in equations 10 and 11). Previously, only 1:5-shifts of the CCl_3 group were known.[6,8] To date, no example of a 1:2-shift of a trichloromethyl group is known.[16]

It is of interest to explore the reasons why III yields IV (quantitatively) with phosphorus pentachloride (equation 3, aromatization by a 1:3-shift of a CCl_3 group to a side chain), whereas with polyphosphoric acid a mixture of V (56%) and VI (3%) is obtained (equations 10 and 11, aromatization by 1:3-shifts of a CCl_3 group to the ring). According to our recent picture of the mechanism of the reaction of phosphorus pentachloride with ketones,[11] III yields the intermediate XXIII, whereas the polyphosphoric acid (in the presence of the chloride ion) III would yield XVIII.



Thus, XXIII and XVIII are identical except for the nature of the phosphorus-containing moiety. These intermediates are capable of reacting in two different (and competitive) ways: A, by loss of the phosphorus-containing moiety to yield the same chlorocarbonium ion XXIV; and B, by rearrangement of the CCl_3 group to yield XXV and XIX (or XXI), respectively.



Since III yields IV exclusively with phosphorus pentachloride[9] (equation 3) obviously XXIII decomposes entirely by path A to yield XXIV, which then loses a proton to form the semi-benzene XXVI (not isolated) which easily rearranges to IV.[17] On the other hand, XVIII decomposes only by path B (except for a small amount by equation 9). Possibly the explanation lies in the temperature coefficients of the two paths, for the reaction with phosphorus pentachloride was carried out at 0–10° (or at 40° in methylene chloride) whereas the reaction with polyphosphoric acid was run at 80–90° because of the high viscosity of PPA at lower temperatures.

Alternatively, one might suggest that the intermediate XXIII is inherently less stable than XVIII and that XXIII has a greater tendency to lose phosphorus oxychloride and chloride ion than XVIII has to lose the polyphosphoric acid anion. Further work is required before this point can be established.

Another point of interest lies in the fact that on treatment with polyphosphoric acid I yields 4-chloro-2-methylbenzoic acid (VIII) (equation 5) whereas on similar treatment, III yields 2-chloro-4,5-dimethylbenzoic acid (V) (equation 4). Both reactions presumably go through the same type of intermediate, XIII and XVIII, respectively, yet the former results in a 1:2-shift of a methyl group whereas the latter results in a 1:3-shift of a trichloromethyl group. We believe that the extra methyl group in III (XVIII) is responsible as it exerts a steric strain which is more easily reduced by a 1:3-shift of a CCl_3 group than it would be by a 1:2-shift of a methyl, especially since the 1:2-shift would have to be preceded by the loss of the phosphorus-containing moiety to form the carbonium ion XIV.

Experimental[18]

3,4-Dimethyl-4-trichloromethyl-2,5-cyclohexadienone (III).[9]—In the best of many experiments in which the yield varied from 54–77%, a solution of 61 g. (0.5 mole) of 3,4-dimethylphenol in 300 ml. of carbon tetrachloride was added during 30 minutes to a stirred slurry of 133 g. of anhydrous aluminum chloride in 300 ml. of carbon tetrachloride, keeping the mixture at 5–20° while a slow stream of dry nitrogen swept the hydrogen chloride formed into traps containing measured amounts of sodium hydroxide solution. After two hours 0.4 mole of acid had been evolved and the reaction mixture was poured on 1.5 l. of ice containing 100 ml. of concentrated hydrochloric acid. After thorough (30 min.) decomposition of the reaction complex (stirring) the organic phase was collected, washed with water and 10% sodium hydroxide, and worked up in the usual manner.[19] The resulting brown oil partly crystallized to yield 43.1 g. of crude III. Superheated steam distillation at 130° (43 l.) yielded 49.0 g. of III, m.p. 57.0–60.5°. Recrystallization from benzene yielded 86.5 g. (72.5%) of colorless III, m.p. 60.0–61.0°; infrared absorption at 5.98, 6.10 and 6.20 μ.

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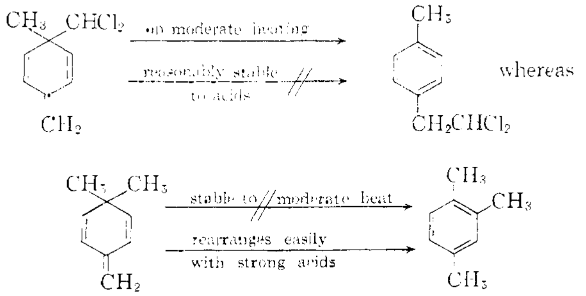
(16) See ref. 7. Work by Mr. John Eberwein has just proved that another reported 1:2-shift of a trichloromethyl group does not occur; see H. Plieninger and G. Keilich, *Ber.*, **91**, 1893 (1958).

(17) K. von Auwers and K. Ziegler, *Ann.*, **425**, 232 (1921), have pointed out the contrasting behaviors of chlorinated and non-chlorinated semi-benzenes on treatment with strong acids and with heat. The examples below are typical.



Compounds containing the CCl_3 group behave analogously, although their behavior has not been studied exhaustively (see refs. 6 and 8, this paper).

(18) All melting points are corrected. All distillations were done through an 8-inch column, 0.5 inch in diameter, packed with 1/8 inch glass helices. All boiling points are uncorrected. All microanalyses by Galbraith Laboratories, Knoxville, Tenn., unless otherwise noted.

(19) Worked up in the usual manner means that the organic layer (in most cases in a 1:1 ether–benzene mixture) was washed with saturated sodium chloride solution and then filtered through a funnel containing anhydrous magnesium sulfate into a flask in which the solvents were largely removed under reduced pressure.

The red 2,4-dinitrophenylhydrazone, m.p. 166.5–167.5°, was prepared in the usual manner and purified by chromatographing over alumina.

Anal. Calcd. for $C_{15}H_{14}Cl_3N_4O_4$: N, 13.3. Found: N, 13.6.

4-Methyl-3-(β,β,β-trichloroethyl)-chlorobenzene (IV).—When 24.0 g. of III was added in portions to 21.0 g. of phosphorus pentachloride an immediate exothermic reaction, accompanied by evolution of hydrogen chloride, began. After 30 min. the reaction mixture was heated under vacuum on the steam-bath to remove the phosphorus oxychloride. On heating a small amount of the residual oil with concentrated sulfuric acid the lack of evolution of hydrogen chloride indicated that no benzotrichloride grouping was present. Vacuum distillation of the oil yielded IV, b.p. 121–128° at 4 mm., in 88.5% yield. On cooling and standing colorless crystals of IV, m.p. 35.0–36.1°, separated.[20]

Anal. Calcd. for $C_9H_8Cl_4$: C, 41.9; H, 3.1; Cl, 55.0. Found: C, 41.5; H, 3.2; Cl, 55.0.

Proof of Structure of IV.—a. Oxidation of 1.8 g. of IV was carried out by heating in a solution of 6 g. of potassium permanganate, 10 ml. of water and 20 ml. of pyridine on a steam-bath for 6 hours. Another 6 g. of permanganate was added and heating was maintained for another 6 hours. After a conventional work-up 0.47 g. (48%) of 4-chlorophthalic acid, m.p. and mixed m.p. with an authentic sample, 149–150°, was obtained.

b. Oxidation of 1.3 g. of IV by heating for 12 hours on a steam-bath with a solution of 1.5 g. of sodium dichromate, 2 ml. of concentrated sulfuric acid, 15 ml. of water and 70 ml. of acetic acid afforded 1.34 g. (93%) of 4-chloro-2-(β,β,β-trichloroethyl)-benzoic acid, m.p. 165.0–169.0°. The analytical sample[9] melted at 168.0–169.5°.

c. A solution of 3.44 g. of sodium ethoxide in 50 ml. of absolute ethanol was added during 3 hours to a stirred solution of 38.5 g. of IV in 50 ml. of alcohol at room temperature. Distillation of the product from this reaction mixture yielded 2.13 g. of a fraction, b.p. 88–89° at 4 mm., n^{25}D 1.5594, which was undoubtedly **3-(β-chloroethynyl)-4-methylchlorobenzene**, because of a strong absorption band at 4.6 μ and the absence of an acetylenic hydrogen band in the 3.0 μ region.

Anal. Calcd. for $C_9H_6Cl_2$: Cl, 38.4. Found: Cl, 38.1.

d. Addition of a drop of this chloroacetylene to alcoholic silver nitrate yielded a precipitate of silver chloride immediately, and oxidation with alkaline permanganate as above yielded 4-chlorophthalic acid.

In addition to the chloroacetylene, 13.5 g. (41%) of 3-(β,β-dichlorovinyl)-4-methylchlorobenzene, b.p. 101–106°, was obtained. and redistillation through a 12-inch spinning band column[21] yielded the pure compound.[9] b.p. 114.5–115.5°, n^{20}D 1.5828.

e. On addition of a solution of 3.2 g. of potassium permanganate in 15 ml. of pyridine and 25 ml. of water to a stirred solution of 2.2 g. of the above trichloro compound in 25 ml. of pyridine an exothermic reaction ensued. Within 5 minutes the reaction was complete and 1.05 g. (62%) of 5-chloro-2-methylbenzoic acid (see below for proof of structure), m.p. 169.5–171.0°, was obtained. The same acid was obtained in 41% yield by ozonization of the trichloro compound in acetic acid.

f. The above chloromethylbenzoic acid was subjected to the Schmidt reaction,[22] and the resulting amino compound was deaminated.[23] The resulting chlorotoluene was oxidized by refluxing with excess potassium permanganate in pyridine–water for 9 hours to yield *p*-chlorobenzoic acid, m.p. and mixed m.p. with an authentic sample, m.p. 240–242°, in 45% over-all yield. This acid was also converted to the amide, m.p. alone and mixed with authentic *p*-chlorobenzamide, 177.5–179.0°. In conjunction with the fact that this chloromethylbenzoic acid was converted to 4-chlorophthalic acid on oxidation with potassium permanganate, the structure is established as 5-chloro-2-methylbenzoic acid.

Treatment of III with Polyphosphoric Acid.[10]—A mixture of 48.0 g. of III and 77 g. of PPA[10] at 80–95° was stirred for 5 hours. All gases evolved were continuously swept out with nitrogen into traps containing aniline in benzene. During the early stages there was copious evolution of gas, but after 5 hours no appreciable quantity of gas was being evolved. The cooled reaction mixture separated into two phases. The heavier phosphoric acid layer was extracted with three 200-ml. portions of ether which were added to the upper organic layer. The PPA layer was then diluted with 500 ml. of water and extracted with three 50-ml. portions of ether. The total ether layer was worked up as usual[19] to yield a yellow oil which was distilled to yield the following fractions: 1, b.p. 105–107° at 55 mm. (4.6 g.); 2, b.p. 95–98° at 0.5 mm. (1.3 g.); 3, b.p. 98–102° at 0.5 mm. (10.0 g.); and a solid residue of 12.5 g.

Fraction 1 proved to be 3,4-dimethylchlorobenzene (VII) (16%).

Anal. Calcd. for C_8H_9Cl: C, 68.6; H, 6.5; Cl, 25.4. Found: C, 68.4; H, 6.5; Cl, 25.0.

Oxidation with excess potassium permanganate as above yielded 4-chlorophthalic acid, m.p. 149.5–151.0°, in 60% yield.

Fraction 2 was an acid chloride which on hydrolysis yielded 1.1 g. of acid, m.p. 128.0–135.5°. On recrystallization, a small amount of purer acid, m.p. 143.0–144.5°, was obtained. In another run, the entire acid fraction was esterified with methanol. The unesterified portion of acid was refluxed with methanol and sulfuric acid twice more. The final free acid fraction on one crystallization from benzene yielded pure VI, m.p. 147.0–148.0°.

Anal. Calcd. for $C_9H_9ClO_2$: C, 58.6; H, 4.9; Cl, 19.3. Found: C, 58.4; H, 4.8; Cl, 19.0.

This acid was proved to be 2-chloro-5,6-dimethylbenzoic acid (VI) as shown below.

Fraction 3 solidified on cooling (m.p. 59–63) and proved to be an acid chloride (absorption at 5.70 μ). Hydrolysis yielded 8.4 g. of crude V, m.p. 175–180°. Recrystallization from benzene afforded 8.0 g. of colorless 2-chloro-4,5-dimethylbenzoic acid (V), m.p. 181.0–182.0° (for proof see below).

Anal. Calcd. for $C_9H_9ClO_2$: C, 58.6; H, 4.9; Cl, 19.3. Found: C, 58.4; H, 4.8; Cl. 19.0.

By dissolving the pot residue in alkali, extracting this solution with ether, and acidifying the aqueous layer, an additional 12.1 g. of V was obtained. In all about 56% of V and 3% of VI was obtained.

When extra hydrogen chloride was added to the PPA before reaction with III, the yield of acids V and VI was increased to about 67% and the amount of VII produced was cut to about 13% (average of two experiments in which the isolation procedure was the same as that described above).

On treatment of a small amount of pure V with thionyl chloride, the pure acid chloride, m.p. 63.0–64.0°, was obtained. The infrared spectrum was identical to that obtained from the crude acid chloride above (fraction 3).

In the trap which contained aniline in benzene there was a white precipitate which was collected. On washing with water, the aniline hydrochloride dissolved to leave 8.4 g. (equivalent to a 20% yield of phosgene) of *sym*-diphenylurea, m.p. and mixed m.p. with authentic sample, 238–240°.

Proof of Structure of Acids V and VI.—a. Treatment of V as above in the case of 5-chloro-2-methylbenzoic acid[22,23] yielded crude 3,4-dimethylchlorobenzene which on oxidation yielded 4-chlorophthalic acid in 48% over-all yield from V. Reduction of V with lithium aluminum hydride in ether afforded 2-chloro-4,5-dimethylbenzyl alcohol, m.p. 95.0–96.0°, in over 80% yield.

Anal. Calcd. for $C_9H_{11}ClO$: C, 63.4; H, 6.5; Cl, 20.8. Found: C, 63.6; H, 6.5; Cl, 20.7.

A solution of 2.0 g. of this alcohol in 25 ml. of benzene was kept saturated with dry hydrogen chloride at room temperature for 14 hours. Distillation of the dark oil as produced yielded 0.5 g. (22%) of yellow oil, b.p. 115–125° at 8 mm., and a large residue of non-volatile polymer. This yellow oil was reduced with excess lithium aluminum hydride in refluxing tetrahydrofuran for 6 hours. After the usual treatment 0.30 g. of oil was obtained from which 0.20 g. (50%) of impure 2,4,5-trimethylchlorobenzene, m.p. 60.0–65.0°, was obtained. Further recrystallization from aqueous alcohol afforded 0.15 g. of colorless 2,4,5-trimethyl-

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(20) By running the above reaction in methylene chloride at reflux, Dr. D. Pawellek has obtained a virtually quantitative yield of IV.

(21) Obtained from Nester and Faust. Exton. Pa.

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

(23) According to N. Kornblum, *ibid.*, Vol. II. 1945. p. 262.

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.

COLUMBUS 10, OHIO

[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.

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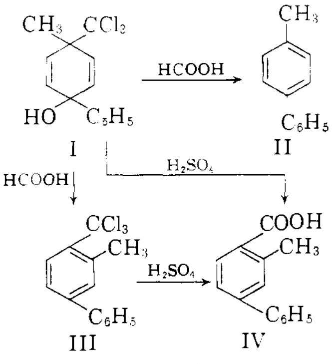
It is shown that in two cases in which a trichloromethyl group was reported to undergo a 1:2-shift, errors in identification of products were made. 4-Methyl-1-phenyl-4-trichloromethyl-2,5-cyclohexadienol (I) yields 4 methylbiphenyl (II) on treatment with cold formic acid, and 2,6-dichloro-4-methyl-4-trichloromethyl-2,5-cyclohexadienol (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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[2] This research was suppoited 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).