Anal. Calcd. for $C_{22}H_{32}ClN$: C, 76.37; H, 9.34; N, 4.05. Found: C, 76.38; H, 9.21; N, 3.98.

Rearrangement of X to form α-(2,4,6-trimethylbenzyl)-2,4,6-trimethylbenzyldimethylamine (XI). This rearrangement was carried out with 24.7 g. (0.0715 mole) of bis(2,4,6-trimethylbenzyl)-dimethylammonium chloride (X) and 0.2 mole of sodium amide in 300 ml. of liquid ammonia essentially as described for the rearrangement of I. The reaction period was 6 hr. The ether insoluble salts were triturated with 100 ml. of water acidified with hydrochloric acid. Removed from this mixture by filtration was 9.2 g. (37% recovery) of quaternary salt X, m.p. 196–197°, mixed m.p. 200–201°.

The neutral fraction was not steam distilled. After evaporation of the ether the solid residue was recrystallized from methanol yielding 0.05 g. (0.5%) of crudel, 2-dimesitylethane, m.p. 100–105°. Two more recrystallizations from methanol raised the melting point to 112–114°, mixed m.p. 114–115°, lit.,[20] m.p. 117–118°.

The mother liquor from the first recrystallization of the dimesitylethane was treated with 2,4-dinitrophenylhydrazine solution and a yield of 0.05 g. (0.2%) of 2,4,6-trimethylbenzaldehyde-2,4-dinitrophenylhydrazone was precipitated, which after one recrystallization from ethanol melted at 246–248°, mixed m.p. 249–250°, lit.,[24] m.p. 250–251°.

From the amine fraction was obtained 12.90 g. (58%) of crude amine, which after one recrystallization from methanol yielded 11.1 g. (50%) of pure α-(2,4,6-trimethylbenzyl)-2,4,6-trimethylbenzyldimethylamine (XI), m.p. 100.5–101°.

Anal. Calcd. for $C_{22}H_{31}N$: C, 85.38; H, 10.10; N, 4.53. Found: C, 85.42; H, 10.30; N, 4.37.

Reaction of the methiodide of XI *with sodium amide in liquid ammonia.* The methiodide of 6.08 g. (0.0195 mole) of amine XI was prepared by refluxing with excess methyl iodide in 100 ml. of acetonitrile for 8 hr. The salt was precipitated with ether. The yield of the crude, dry methiodide was 11.32 g. (70%).

This methiodide, 6.3 g. (0.014 mole), was added to 0.03 mole of sodium amide in 200 ml. of liquid ammonia. After 2 hr. the reaction was quenched with 1.6 g. (0.03 mole) of solid ammonium chloride and the ammonia replaced by ether. The mixture was filtered and the ethereal filtrate was evaporated on a steam bath. After the residue was heated on the steam bath for 0.5 hr. to thermally rearrange any *exo*-methyleneamine present, the residue was cooled, taken up in ether and filtered, and gaseous hydrogen chloride was bubbled through until no more amine hydrochloride precipitated. The mixture was filtered and evaporated, yielding after one recrystallization from a mixture of methanol and ethanol 1.9 g. (51%) of 1,2-dimesitylethylene (XIII), m.p. 131–132°, lit.,[25] m.p. 132–133°. A second recrystallization raised its melting point to 132–132.5°. Admixture with only 5% of 1,2-dimesitylethane, which would have been formed by acidic decomposition of *exo*-methyleneamine XIV, produced a melting point of 126–128°.

The solid amine hydrochloride was stirred with 50 ml. of 3*M* sodium hydroxide and 50 ml. of ether until all solid was dissolved. The ether layer was separated, dried, and evaporated, leaving 0.50 g. (11%) of crude amine, m.p. 60–63°. Three recrystallizations from methanol raised the m.p. to 68–69°. The structure of the amine is assumed to be 2,3-dimesitylpropyldimethylamine (XV).

Anal. Calcd. for $C_{23}H_{33}N$: C, 85.39; H, 10.28; N, 4.33. Found: C, 85.12; H, 9.77; N, 4.04.

Reduction of 1,2-dimesitylethylene (XIII) *to 1,2-dimesitylethane* (VII) *with sodium in liquid ammonia.* A 0.55-g. portion of 1,2-dimesitylethylene was dissolved in 30 ml. of anhydrous ether. A solution of 0.5 g. of sodium in 100 ml. of liquid ammonia was slowly dropped into the stirred solution of hydrocarbon until the blue color of the sodium remained for 10 seconds. The reaction mixture was then quickly treated with 1.0 g. of solid ammonium chloride, the ammonia replaced by ether and the mixture filtered. Evaporation of the filtrate and recrystallization of the residue from methanol yielded 0.50 g. (91%) of 1,2-dimesitylethane, m.p. 117–117.5°, mixed m.p. 117–117.5°, lit.,[22] m.p. 117–118°.

DURHAM, N. C.

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[24] J. C. Lunt and F. Sondheimer, *J. Chem. Soc.*, 1950, 2957.

[25] R. C. Fuson, E. C. Horning, M. L. Word, S. P. Rowland, and J. L. Marsh, *J. Am. Chem. Soc.*, 64, 30 (1942).

[CONTRIBUTION FROM THE HOOKER CHEMICAL CORPORATION RESEARCH LABORATORIES]

A Study of the Acid and Base Hydrolysis of Bridged Ketones Derived from Diels-Alder Adducts of 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene

PAUL E. HOCH

Received November 1, 1960

A series of new Diels-Alder adducts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene have been prepared. The adducts derived from vinyl chloride, ethyl acrylate, ethylene, propylene, and cyclohexene yield the expected bicyclic ketones upon treatment with concentrated sulfuric acid. The 1,2-dichloroethene adduct with sulfuric acid yields pentachlorobenzene. A diene obtained by dehydrohalogenation of the 1,4-dichloro-2-butene adduct undergoes a hydrolytic acid cleavage with sulfuric acid to give 2,3,4-trichloro-5-methylphthalid. Treatment of the bicyclic ketones with alcoholic base results in hydrolytic cleavage of the carbonyl bridge and dehydrohalogenation of the bridge head halogens to yield chlorine containing aromatic acids. An intermediate 2,3,4-trichloro-4a,5,6,7,8,8a-hexahydronaphthoic acid was isolated from the alcoholic base treatment of the bicyclic ketone derived from the cyclohexene adduct.

The Diels-Alder adducts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene with olefinic dieneophiles yield bicyclic bridged ketals of the general structure indicated in Fig. 1. Many such adducts have been reported in the literature.[1,2]

The Diels-Alder adducts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene prepared for this investigation are all new compounds. Physical properties and analysis of these adducts are listed in Table I.

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[1] C. W. Roberts, *Chem. & Ind.*, 110 (1958).

[2] H. E. Ungnade and E. T. McBee, *Chem. Revs.*, 58, 249 (1958).

TABLE I

DIELS-ALDER ADDUCTS OF 1,2,3,4-TETRACHLORO-5,5-DIMETHOXYCYCLOPENTADIENE

Dienophile	Adduct	Reaction Time, hr.	Reaction Temp.	Yield, %	B.P.	Mm.	M.P.	n^{25}_{D}	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
cis 1,2-Dichloroethene	I	20	87-150	15	142	0.8	111-112	—	—	—	—	—	58.7	58.2
cis 1,4-Dichloro-2-butene	III	20	135	48	155	1.0	—	1.5563	33.97	33.69	3.09	2.97	54.7	55.0
Vinyl chloride	VI	6	190	62	89	0.15	37-38	1.5330	—	—	—	—	54.4	54.4
Allyl chloride	VII	60	48-170	32	134	2.5	—	1.5327	—	—	—	—	39.0	39.5
Cyclohexene	XIII	35	86-142	66	138	0.5	81.5-82.3	—	—	—	—	—	40.8	40.6
Ethylene	XVIII	8	180-185	60	56	0.05	—	1.5248	37.03	37.14	3.43	3.38	—	—
Propylene	XXII	6	169	50	59	0.04	—	1.5190	39.26	38.87	3.92	4.00	46.3	46.6
Ethyl acrylate	X	6	145	86	133	0.18	—	1.5123	—	—	—	—	39.0	39.5

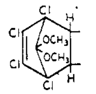

Figure 1

The original purpose of this work was to study the effect of a base such as alcoholic potassium hydroxide on the bicyclic bridged ketones derived from the bridged ketals above. It was hoped that the base would hydrolytically cleave the ketone to an acid, a reaction studied extensively by Allen.[3] Excess base would simultaneously cause aromatization of the system by removal of both bridge head halogens through dehydrohalogenation (Fig. 2).

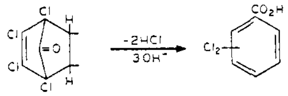

Figure 2

The conversion of the bridged ketal to the ketone in this class of compounds has been successfully accomplished by McBee *et al.*[4] with concentrated sulfuric acids at room temperature. The ketones were readily isolated in good yields with no side products reported Newcomer and McBee[5] observed earlier, however, that the maleic anhydride adduct upon treatment with concentrated sulfuric acid at elevated temperatures (80°) did not yield the ketone but instead yielded 1,2,3-tricarboxy-4,5-dichlorobenzene, which indicated acid cleavage of the bridged ketone formed with loss of hydrogen chloride (Fig. 3).

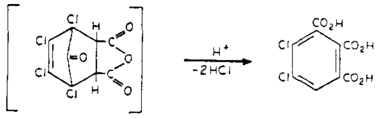

Figure 3

Treatment of the ketal adducts prepared in this study (Table I) with concentrated sulfuric yielded the bridged ketones or their hydrates with several exceptions.

The ketal adduct derived from *cis*-1,2-dichloroethene(7,7 - dimethoxy - 1,2,3,4,5,6 - hexachlorobicyclo[2.2.1]heptene - 2) I, upon treatment with concentrated sulfuric acid did not appear to react at the normal experimental temperature used in the study (35–50°). This may have been due to the low solubility of the solid in the acid. Raising the temperature of the stirred suspension to 80° caused a change in the physical state of the solid and the

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[3] C. F. H. Allen, *Chem. Rev.*, **37**, 209 (1945).

[4] E. T. McBee, W. R. Diveley, and J. E. Burch, *J. Am. Chem. Soc.*, **77**, 385 (1955).

[5] J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 949 (1949).

liberation of hydrogen chloride. The solid isolated from this reaction was identified as pentachlorobenzene. Obviously the ketone formed decarbonylated at this elevated temperature and loss of hydrogen chloride caused aromatization (Fig. 4).

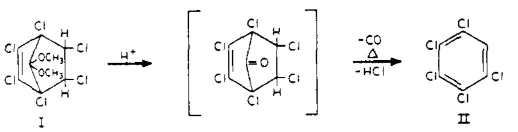

Figure 4

The ketal adduct derived from *cis*-1,4-dichlorobutene-2-(7,7-dimethoxy-1,4,5,6-tetrachloro-2,3-bis(chloromethyl)bicyclo[2.2.1]heptene-5) III, readily dehydrohalogenates upon treatment with alcoholic potassium hydroxide to give the exocyclic diene (7,7-dimethoxy-1,4,5,6-tetrachloro-2,3-bis(methylene)bicyclo[2.2.1]heptene-5) IVa, (m.p. 105–106°). This diene is analogous to that derived from the Diels-Alder adduct of hexachlorocyclopentadiene and *cis*-1,4-dichlorobutene-2 reported by Hoch and Clegg.[6]

Compound IVa upon treatment with concentrated sulfuric acid at room temperature released hydrogen chloride. This reaction mixture yielded a solid product V (m.p. 236–237°). The chlorine analysis of V corresponds to 2,3,4-trichloro-5-methylphthalide the structure proposed for the product. Infrared analysis indicates a carbonyl absorption 5.69 μ, aromatic unsaturation 6.34 μ, methyl saturate hydrogen 3.45 μ, no aromatic hydrogen 3.3 μ. The ultraviolet spectra show a maxima at 3025 mμ. The compound dissolves slowly in warm base. The resulting solution upon acidification regenerates the starting material. A proposed mechanism[7] for the formation of compound V is indicated in Fig. 5.

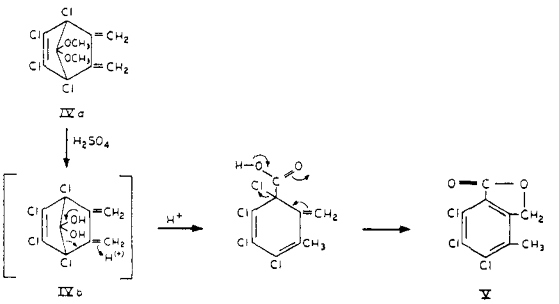

Figure 5

An attempt was made to prepare other ketals with unsaturation *beta* to the bridge to observe the effect of sulfuric acid. The vinyl chloride VI and the allyl chloride adduct VII of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene were prepared (see Table I) and treated with refluxing 15% alcoholic potassium hydroxide to effect dehydrohalogenation. Surprisingly enough neither of these adducts yielded the expected olefins; they were recovered unchanged even upon refluxing overnight. These results are in marked contrast to the manner with which the vinyl chloride[1,2] and allyl chloride[8] adducts of hexachlorocyclopentadiene dehydrohalogenate to the olefins. It is also in contrast to the manner in which III dehydrohalogenates to form the diene IV as discussed previously.[9]

The adduct VI (7,7-dimethoxy-1,2,3,4,5-pentabicyclo[2.2.1]heptene-2) upon treatment with sulfuric acid yielded a solid ketone (7-keto-1,2,3,4,5-pentachlorobicyclo[2.2.1]heptene-2) VIII, m.p. 55.5–57.5°. The ketone reacts exothermically with alcoholic potassium hydroxide to give good yields (85–90%) of 2,3,4-trichlorobenzoic acid IX. The crude acid (m.p. 186–188°) melted only two degrees lower than that reported in the literature (189°).[10] The acid was characterized by elemental analysis, neutral equivalent, melting point and comparison of its infrared spectrum with that of a known sample of the acid. Electronic transformations leading to IX are suggested in Fig. 6.

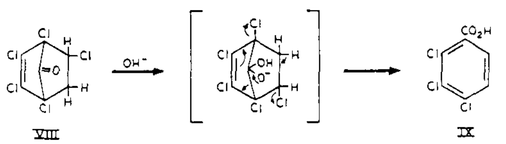

Figure 6

The ethyl acrylate adduct of ketal, (1,4,5,6-tetrachloro-7,7-dimethoxy-2-carbethoxybicyclo-[2.2.1]heptene-5) X when treated with sulfuric acid at 35° yielded an oil which crystallized on standing. This solid had the proper chlorine analysis for a monohydrate of the expected ketone, (7-keto-1,4,5,6-tetrachloro-2-carbethoxybicyclo-[2.2.1]heptene-5) XI (m.p. 101–102°). Refluxing alcoholic base converted XI to a dichlorophthalic acid XII (m.p. 305–306°). The melting point of XII which constituted the major product in the reaction excluded its structure as being that of an *o*-dichlorophthalic acid. These acids all have melting points of 200° and below.[19] The terephthalic acids were excluded on the basis of the structure of the starting materials. Isophthalic acid derivatives remained the only possibility. The melting point of 4,6-dichloroisophthalic acid XIIa is reported as 286°.[10] In a series of preparations in this work the lowest melting point of the crude acid mixture ob-

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(6) Paul E. Hoch and John M. Clegg, *J. Am. Chem. Soc.*, **81**, 5413 (1959).

(7) An alternative mechanism would be a simple allylic shift of the α-halogen with subsequent lactonization.

(8) Unpublished work by the author.

(9) These observations are probably the result of replacing the chlorine atoms on the bridge with the larger methoxyl groups. The enhanced steric shielding makes the approach of the base more difficult for the elimination reaction.

(10) E. Huntress, *Organic Chlorine Compounds*, John Wiley & Sons Inc., New York, 1948.

served was 270-290°. This suggests that some 4,6-isomer could have been formed. No attempt was made to isolate minor products. The major component by elimination is the 4,5-dichloroisophthalic acid. No reference to this isomer was found in the literature (Fig. 7).

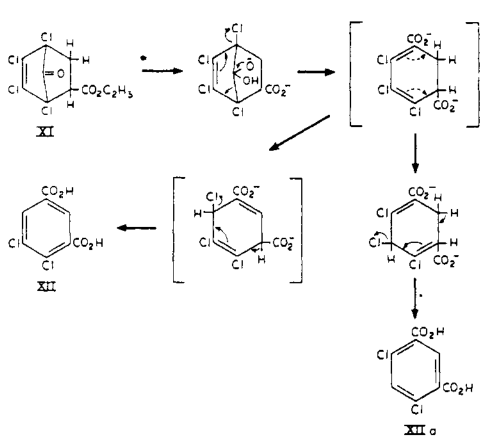

Figure 7

Treatment of the cyclohexene adduct XIII with sulfuric acid yielded a solid ketone (m.p. 208.5–210°) XIV. The alcoholic base treatment, however, led to a surprising observation. A high melting solid XV (m.p. 208.5–210°) was isolated from the reaction mixture whose analysis indicated that an intermediate trichlorohexahydronaphthoic acid had formed. Compound XV when treated overnight with alcoholic caustic formed another mole of salt and a mixture of acids XVI, XVII, m.p. 140–155°, was isolated. Repeated recrystallization did not effect separation nor appreciably alter the melting point of this crude acid mixture. The elemental analysis and the neutral equivalent for these products indicated that a mixture of tetrahydrodichloronaphthoic acids had been formed. A proposed mechanism for their formation is indicated in Fig. 8.

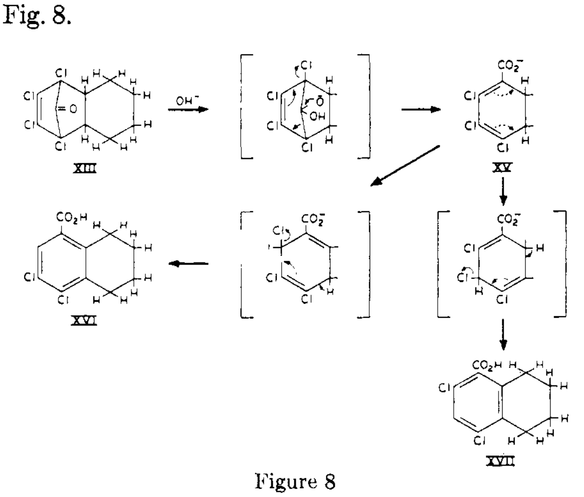

Figure 8

In order to shed some light on the distribution of isomers in the base cleavage reaction the ethylene and propylene adducts were studied.

The ethylene adduct XVIII yielded a solid ketone XIX m.p. 51–54° upon treatment with sulfuric acid. However, a low chlorine analysis coupled with the appearance of water in refluxing benzene suggested the material was a polyhydrate. Repeated recrystallization from benzene finally gave a sharp melting (98°) solid whose analysis agreed with the expected ketone. The ketone decarbonylated around 105–110° (20 mm.) to yield a liquid b.p. 64–66° (0.1 mm.) which presumably was the tetrachlorocyclohexadiene, although the chlorine analysis was low for such a product. An attempt to prepare a Diels-Alder adduct of the diene with maleic anhydride yielded starting materials. Warming XIX to 127–130° (20 mm.) caused decarbonylation and loss of hydrogen chloride. The product was identified through infrared standards as 1,2,3-trichlorobenzene of high purity.

The ketone XIX treated with refluxing alcoholic potassium hydroxide and worked up in the previously described manner yielded a mixture of dichlorobenzoic acids, m.p. 140–180°. Conversion of the crude acid mixture to the acid chlorides with thionyl chloride (without purification) and subsequent comparison with infrared standards available in our laboratories indicated the mixture consisted of 80 ± 5% 2,4-dichlorobenzoyl chloride and 20 ± 5% 3,4-dichlorobenzoyl chloride. There was no indication of other acid chlorides.

These observations suggest the possibility that a diene of the general structure indicated for the cyclohexene adduct is the intermediate in this reaction. Elimination of the other mole of hydrogen chloride then can be pictured as occurring by a 1,4-elimination after an allylic shift of the diene system. The allylic rearrangement can occur in two ways. Subsequent 1,4-elimination can give either the 3,4-(XX) or the 2,4-dichlorobenzoic acid (XXI).

The propene adduct XXII also yielded a solid ketone hydrate upon treatment with sulfuric acid. Preparation of the anhydrous ketone XXIII m.p. 57–59° was accomplished by repeated recrystallization from benzene. The alcoholic base treatment produced a solid which was again a mixture, m.p. 140–180°. Recrystallization from cyclohexane raised the melting point but did little to separate isomers. The chlorine analysis, neutral equivalent, etc., for the crude solid indicated that it was a mixture of dichlorotoluic acids. Oxidation of the crude dichlorotoluic acids with alkaline permanganate gave compound XII as the major product. This indicated that the dominant isomer was probably 4,5-dichlorotoluic acid XXIV. It is obvious, however, that 5,6-dichlorotoluic acid would yield 4,5-dichloroisophthalic acid upon oxidation also. In order to place the structure on somewhat firmer ground the crude dichlorotoluic acid was decarboxylated by a five-step synthesis to the dichlorobenzoic acids. This was accomplished by converting the acids to acid chlorides, the acid chlorides to the amide, the amides by Hoffman rearrangement to the dichlorotoluidines, the toluidines by diazotization and hypophosphorous acid reduction to dichlorotoluenes. The intermediate products were isolated in each case but not purified. Subsequent oxidation of the dichlorotoluenes to dichlorobenzoic acids and conversion of these acids to the acid chlorides for infrared analysis indicated that the mixture contained 2,3-dichlorobenzoic acid as the major component (80 ± 10%) with a small amount 15 ± 5% of 3,4-dichlorobenzoic. This was further proof that the dominant isomer obtained above was 4,5-dichlorotoluic acid (Fig. 9).

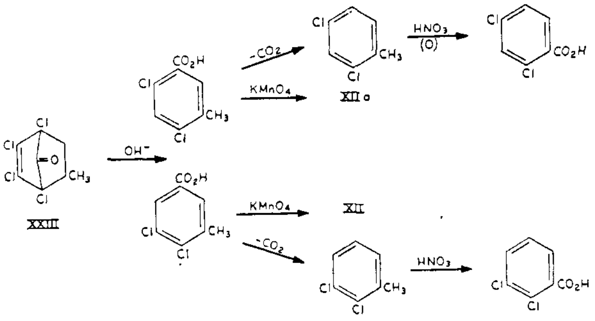

Figure 9

The general reaction sequence reported here has been successfully extended to adducts of higher olefins to yield dichloroalkylbenzoic acids in good yields. An intermediate trichlorodienoic acid apparently similar to that isolated with cyclohexene was isolated in only one other instance and that was with dodecene. This work is not included in experimental detail in this paper because of the lack of data pinpointing the position of the alkyl groups on the ring.

EXPERIMENTAL[11]

Starting materials. Hexachlorocyclopentadiene was converted to 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene by the method of Newcomer and McBee.[6]

Preparation of the Diels-Alder adducts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene. The liquid dieneophiles were mixed in equal molar quantities with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and heated with stirring to reflux. As the lower boiling dieneophiles reacted the pot temperature was permitted to rise to the maximum pot temperature indicated in Table I. The reaction temperature and time of reaction for other dieneophiles are listed in Table I. The adducts from gaseous dieneophiles were prepared by passing the gas at atmospheric pressure into the rapidly stirred ketal heated to 185–200° for the number of hours indicated in Table I. The physical properties and analysis of the adducts are listed in Table I.

Preparation of 7,7-dimethoxy-1,4,5,6-tetrachloro-2,3-bis-(methylene)bicyclo[2.2.1]heptane-5 (IVa). A solution of alcoholic potassium hydroxide was prepared from 40 g. (0.6 mole) of potassium hydroxide (85%) and 380 ml. of ethanol (anhydrous). This solution was stirred and heated to 60°. Into this solution was added a solution of 97 g. (0.25 mole) of 7,7 - dimethoxy - 1,4,5,6 - tetrachloro - 2,3 - bis(chloromethyl)bicyclo[2.2.1]heptene-5 dissolved in 130 ml. of anhydrous ethanol. The reaction was exothermic and the temperature was permitted to rise to 74°. The addition was completed in 45 min. The suspension was stirred an additional 2 hr. at 74°. The alcohol suspension was cooled to 15° and the salt and a crystalline solid that had formed were collected on a filter. The salt was separated from the organic product by triturating the material several times in 100-ml. portions of water. The organic material was air-dried overnight and weighed 42 g., m.p. 93–95°. Recrystallization of this solid several times from ethanol yielded 38 g. (48%) of product, m.p. 98–99°. The material polymerized upon heating at its melting point.

Anal. Calcd. for $C_{11}H_{10}Cl_4O_2$: Cl, 44.8. Found: Cl, 44.9.

Preparation of 2,3,4-trichloro-5-methyl phthalide (V). To 13.5 g. (0.43 mole) of compound IVa was added 50 ml. of concd. sulfuric acid. This suspension was stirred rapidly at room temperature. Hydrogen chloride gas evolved immediately. Upon stirring 1.5 hr., the reaction mixture was poured into ice and the solid weighing 10 g. was collected. This solid recrystallized from an ethanol-benzene mixture weighing 8.0 g. (73%), m.p. 235.5–236.5°.

Anal. Calcd. for $C_9H_5Cl_3O_2$: Cl, 42.3. Found: Cl, 42.1.

Preparation of 7-keto-1,2,3,4,5-pentachlorobicyclo[2.2.1]heptene-2 (VIII). A suspension of 15 g. (0.046 mole) of VII and 40 ml. of concd. sulfuric acid was stirred at 60° for 3.0 hr. and poured into 100 ml. of ice and water. The resulting suspension was extracted with 75 ml. of ether. The ether solution after a water wash was dried over anhydrous magnesium sulfate stripped of solvent to give 11.0 g. (88%) of an oily solid. Several recrystallizations from cyclohexane gave a solid, m.p. 52–54°.

Anal. Calcd. for $C_7H_3Cl_5O$: Cl, 63.2. Found: Cl, 63.3.

Preparation of 2,3,4-trichlorobenzoic acid (IX). A solution of 7.5 g. (0.027 mole) of the crude ketone (VIII) in 25 ml. of absolute ethanol was added portion-wise over 5 min. to a well stirred refluxing solution of 7.2 g. (0.11 mole) of potassium hydroxide (85%) in 50 ml. of absolute ethanol. The suspension was stirred at 75–78° for 15 min., cooled, and the salt removed by filtration. After removing the ethanol under reduced pressure 75 ml. of water was added and this solution was acidified with dilute hydrochloric acid (1:1). The solid resulting was washed with water and dried under vacuum at 100° to yield 6.1 g. (82%) of product, m.p. 185–188°. The material by infrared analysis was 90 ± 5%, 2,3,4-trichlorobenzoic acid. Recrystallization from benzene yielded 5.0 g. solid, m.p. 188–189° (lit., m.p. 188°). A small amount of this acid was converted to the acid chloride with thionyl chloride to yield a solid, m.p. 65–66°, lit.[12] m.p. 64–65°.

7-keto-1,4,5;6-tetrachloro-2-carbethoxybicyclo[2.2.1]heptene-5 (X). A suspension of 20 g. (0.082 mole) of X and 80 ml. of concd. sulfuric acid was vigorously stirred for 5.0 hr. at 35°. The solution was poured into 100 g. of ice water and the organic material extracted with three 50-ml. portions of methylene chloride. After washing the methylene chloride solution twice with 50 ml. of water it was dried over anhydrous magnesium sulfate. The methylene chloride was removed under reduced pressure to yield 22.8 g. (83%) of oil which solidified upon standing overnight. Recrystallization of the solid from chlorobenzene with one Darco treatment yielded 8 g. of solid m.p. 92–93.5°. Recrystallization from benzene gave 6 g. of solid, m.p. 101–102°.

Anal. Calcd. for $C_{10}H_8Cl_4O_4 \cdot H_2O$: C, 35.78; H, 3.06; Cl, 42.19. Found: C, 35.69; H, 3.07; Cl, 42.15.

4,5-Dichloroisophthalic acid (XII). A solution of 5.8 g. (0.017 mole) of the crude ketone X in 30 ml. of absolute ethanol was added during 3 min. to a well stirred solution of 5.3 g. (0.08 mole) of potassium hydroxide (85%) in 100 ml. of absolute ethanol at 50–60°. The suspension was stirred 10 min. cooled, filtered to remove salt, and the alcohol removed under reduced pressure. The residue was dissolved in 150 ml. of water and the solution acidified with dilute hydrochloric

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[11] Chlorine analysis were carried out in the Hooker Laboratories. Infrared spectra were run on a Beckmann Model IR-4. Melting points are uncorrected.

acid (1:1). The solid suspension was chilled 1 hr., filtered, and the solid washed with water. The air dried solid weighed 3.5 g., m.p. 278–290°. Recrystallization from acetic acid gave 2.5 g. (63%) of the product m.p. 305–306°.

Anal. Calcd. for $C_8H_2Cl_2O_4$: Cl, 30.28; neut. equiv., 117. Found: Cl, 29.94; neut. equiv., 117.

9-Keto-1,2,3,4-tetrachloro-1,4,4a,5,6,7,8,8a-octahydronaphthalene (XIV). A suspension of 15 g. (0.043 mole) of XIII and 40 ml. of concd. sulfuric acid was stirred rapidly at 30–34° for 1.5 hr. and 1.0 hr. at 40. The reaction mixture was poured into 200 ml. of water and 12.5 g. (96%) of a waxy solid was isolated. The solid recrystallized several times from cyclohexane gave 5.0 g. of product, m.p. 89.2–90.2°.

Anal. Calcd. for $C_{11}H_{10}Cl_4O$: C, 44.04; H, 3.33. Found: C, 44.20; H, 3.29.

2,3,4-Trichloro-4a,8a,5,6,7,8-hexahydro-1-naphthoic acid (XV). A solution of 1.7 g. (0.0057 mole) of purified compound (XIV) in 5 ml. of absolute ethanol was added to a well stirred solution of 1.5 g. (0.023 mole) of potassium hydroxide (85%) dissolved in 15 ml. of absolute ethanol. The addition made at 40° was completed in 3 min. and stirring at 40–50° was continued 0.5 hr. The alcohol was removed under reduced pressure and the residue dissolved in 15 ml. of water and filtered. The filtrate was acidified with dilute (1:1) hydrochloric acid, chilled several hours, and then filtered. The solid obtained weighed 0.8 g. (50%). Recrystallization from chlorobenzene yielded 0.6 g. solid, m.p. 208.5–210°.

Anal. Calcd. for $C_{11}H_{11}Cl_3O_2$: C, 46.77; H, 4.25; Cl, 37.66; neut. equiv., 281.5. Found: C, 47.08; H, 4.01; Cl, 37.2; neut. equiv., 278.

Preparation of dichlorotetrahydro-1-naphthoic acids (XVI, XVII). A solution of 1.5 g. (0.027 mole) of potassium hydroxide (85%) in 20 ml. of absolute ethanol was warmed to reflux with stirring. To this solution was added 1.7 g. (0.0057 mole) of XV, during 2 min. The suspension was refluxed for an additional 8 hr., cooled, and filtered. The ethanol was removed from the filtrate under vacuum and the pasty residue treated with 10 ml. of water. A very small amount of water insoluble solid was removed by filtration and the filtrate was acidified with hydrochloric acid (1:1). The gummy solid resulting upon acidification was washed with water, air-dried overnight, then taken up in refluxing cyclohexane. A crystalline solid weighing 0.25 g. (18%), m.p. 132–145°, was recovered. Several recrystallizations from cyclohexane and then benzene raised the melting point to 145–158°.

Anal. Calcd. for $C_{11}H_{10}Cl_2O_2$: C, 53.91; H, 4.08; Cl, 28.95; neut. equiv., 245. Found: C, 54.07; H, 4.04; Cl, 28.87; neut. equiv., 246.

1,2,3,4-Tetrachloro-7-keto-bicyclo[2.2.1]heptene-2 (XIX). A mixture of 71 g. (0.24 mole) of compound (XVIII) and 140 ml. of concd. sulfuric acid was stirred for 1 hr. at 30–35°. Solid separated within 1 min. and formed in quantity throughout the reaction. The suspension was poured into ice and water. The solid was collected by filtration and upon air drying overnight weighed 67 g. This polyhydrate was placed under vacuum and warmed in an oil bath at 110° for 2 hr. The solid obtained was recrystallized three times from benzene and vacuum dried overnight at 60° to give 50 g. (84%) of product, m.p. 96.5–97.5°.

Anal. Calcd. for $C_7H_4Cl_4O$: Cl, 57.7. Found: Cl, 57.5.

Preparation of 2,4- and 3,4-dichlorobenzoic acid (XX, XXI). A solution of 8.0 g. (0.13 mole) potassium hydroxide (86%) in 75 ml. of absolute ethanol was prepared and warmed to 60–65°. To this solution was added portion-wise 7.7 g. (0.031 mole) of compound XIX over a period of 1–2 min. The suspension was stirred at reflux for 2 hr. cooled, and filtered. The filtrate was subjected to a vacuum stripping and the residue was dissolved in 50 ml. of water. The solution was acidified with dilute (1:1) hydrochloric acid and the suspension resulting was chilled then filtered. The solid after air-drying several days weighed 3.5 g. (59%), m.p. 153.6–154.8°. This solid was recrystallized twice from nitromethane to yield 1.7 g. solid, m.p. 154–156°.

Anal. Calcd. for $C_7H_4Cl_2O_2$: C, 43.79; H, 2.60. Found: C, 43.71; H, 2.31.

A 1.0-g. portion of the recrystallized acid above was refluxed with 4 ml. of thionyl chloride for 3 hr. The thionyl chloride was removed and the residue submitted for an infrared analysis against standards for dichlorobenzoyl chlorides. The results indicated 80 ± 5% 2,4-dichlorobenzoyl chloride and 15 ± 5% 3,4-dichlorobenzoyl chloride. There was no measurable indication of the 2,5- or the 2,3-dichlorobenzoyl chloride isomers.

Preparation of 1,2,3,4-tetrachloro-5-methyl-7-keto-bicyclo[2.2.1]heptene-2 (XXIII). A suspension of 7.0 g. (0.023 mole) of the propene adduct (XXII) and 20 ml. of concd. sulfuric acid was stirred vigorously for 1.0 hr. at 45–50°. The suspension was poured into 50 g. of ice and water. The solid that formed was collected on a filter. It was quite hygroscopic and tended to oil on the filter. This material was recrystallized several times from methylcyclohexane with considerable loss to yield a solid (m.p. 57–59°) weighing 2.0 g. (33%).

Anal. Calcd. for $C_8H_6Cl_4O$: C, 36.96; H, 2.31; Cl, 54.58. Found: C, 37.10; H, 2.39; Cl, 54.1.

Preparation of dichlorotoluic acids (XXIV, XXV). A solution of 17.6 g. (0.27 mole) of potassium hydroxide (85%) in 100 ml. of absolute ethanol was prepared and warmed to 60°. To this well stirred solution was added portion-wise over 5 min. 17.0 g. (0.065 mole) of the crude ketone XXIII prepared according to the procedure above. The suspension was refluxed an additional 2.0 hr., cooled, and filtered. The ethanol was stripped from the filtrate under reduced pressure and the residue resulting dissolved in a minimum amount of water. The aqueous solution was acidified with dilute hydrochloric acid (1:1) and the resulting suspension cooled and filtered. The crude air-dried solid weighed 12 g. (96%) and melted over a broad range (140–180°). Recrystallization from cyclohexane gave 7.0 g. of solid, m.p. 172–182°.

Anal. Calcd. for $C_8H_6Cl_2O_2$: Cl, 34.6; neut. equiv., 205. Found: Cl, 34.7; neut. equiv., 204.5.

Oxidation of compounds XXIV, XXV *with alkaline potassium permanganate.* A solution of 4.0 g. (0.02 mole) of the crude dichlorotoluic acids XXIV and XXV, 2.5 g. of sodium carbonate, 0.69 g. (0.0043 mole) potassium permanganate, and 137 ml. of water was refluxed for 18 hr. The precipitated manganese oxide was removed by filtration and the filtrate acidified with concentrated hydrochloric acid. A white solid was collected weighing 0.3 g. (65%), m.p. 305–307°. This product was shown by comparison of infrared spectra to be identical with compound XII, 4,5-dichloroisophthalic acid.

Steps in removal of the carboxyl group in compounds XXIV, XXV to establish the position of the halogens on the toluic acid.

Conversion of XXIV, XXV *to the amides.* A solution of 9.0 g. (0.043 mole) of the crude acids XXIV and XXV and 36 ml. of thionyl chloride was refluxed overnight. The thionyl chloride was stripped under reduced pressure and the residual oil obtained poured into 100 ml. of concd. ammonium hydroxide to yield 6.6 g. (74%) of air-dried solid amides.

Conversion of the amides to the aniline derivatives (*Hoffmann reaction*). A solution of 5.5 g. (0.086 mole) of potassium hydroxide (85%) in 50 ml. of cold water (0°) was treated with 5.8 g. (0.72 mole) of bromine. This solution was poured over 6.6 g. (0.032 mole) of the crude amide isolated above. To this suspension was added 7.7 g. of potassium hydroxide (85%) in 12 ml. of water. This mixture was stirred and the temperature raised slowly with external heating. The mixture was warmed at 75° for 45 min. The oil suspension resulting was extracted several times with 20-ml. portions of ether. The ether solution after drying over anhydrous magnesium sulfate and filtering was treated with an excess of gaseous anhydrous hydrogen chloride. A gray solid weighing 1.6 g. (23%) resulted which was presumably the dichlorotoluidine hydrochlorides.

Conversion of the dichlorotoluidines to dichlorotoluenes. The crude amine mixture obtained above (1.6 g., 0.0075 mole) was stirred in 3 ml. of hydrochloric acid (2:1) and treated at 3° with 0.69 g. (0.0081 mole) of sodium nitrite dissolved in 1.4 ml. of water. After 5 min. of stirring 12.5 ml. of a 50% hypophosphorous acid solution (0°) was added. This mixture was stirred for 15 min., then permitted to stand overnight at 5°. The oily suspension was extracted with 40 ml. of ether and after drying and stripping the solvent 1.1 g. (90%) of a dark oil was isolated. Infrared analysis indicated 3,4-dichlorotoluene was present (3–4%), no 2,4-dichlorotoluene. No standard was available for the 3,4-dichlorotoluene.

Oxidation to dichlorotoluic acids. A suspension of 0.8 g. (0.0049 mole) of the crude dichlorotoluenes obtained above and 20 ml. of nitric acid (2:3) was placed in a sealed tube at 140° for 2 days. The mixture of solids resulting were treated with boiling water to extract the acids. The water yielded 0.33 g. (35%) of solid, m.p. 135–140°. An infrared analysis indicated the mixture contained approximately 85–90% 2,3-dichlorobenzoic acid and 10–15% 2,4-dichlorobenzoic acid.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DEPAUW UNIVERSITY]

Acid-Catalyzed Decarbonylation of 2,4,6-Trimethoxybenzaldehyde Accompanying Condensation Reactions

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At concentrations above approximately $1 \times 10^{-4}M$ 2,4,6-trimethoxybenzaldehyde, I, in mineral acid forms 2,4,6,2′,4′,6′,-2″,4″,6″-nonamethoxytriphenylmethane (II). Kinetic studies showed II to be formed from the condensation of I with 1,3,5-trimethoxybenzene (III) from the normal decarbonylation of I. 2,4,6,2′,4′,6′-Hexamethoxydiphenylcarbinol was obtained from the reaction of I and III in perchloric acid.

In connection with a study of the mechanism of the acid-catalyzed decarbonylation of 2,4,6-trimethoxybenzaldehyde[1] (I) experiments were carried out to identify the product (formic acid) which had its origin in the aldehyde group. For this purpose the concentration of I was necessarily of the order of 1.0×10^{-2} to $2.5 \times 10^{-3}\,M$, compared with concentrations of approximately 2.0 to $6.0 \times 10^{-5}M$ used in all of the kinetic studies. In all of the experiments at the higher concentrations, a red solution, a red precipitate, and absorption at 520–560 mμ were observed. None of these occurred in the kinetic studies. By treatment of the red solid with water, a white solid was obtained. These results were not published pending further research. Nevertheless, we proposed that the white solid was probably 2,4,6,2′,4′,6′,2″,4″,6″-nonamethoxytriphenylmethane (II) resulting from reaction of I with the 1,3,5-trimethoxybenzene (III) formed by decarbonylation of I, and that the red compound was a complex between II and the mineral acid.

The proposed structures of these materials were based principally upon reports that, in acid, aromatic aldehydes reacted readily with 1,3,5-(or 1,2,4-)trimethoxybenzene to form substituted triarylmethanes, which were colored in the acid solution.[2] In one case the triarylmethane was obtained when only the aldehyde was used. Thus, 2,4,5,-2′,4′,5′,2″,4″,5″ - nonamethoxytriphenylmethane was prepared by heating 2,4,5-trimethoxybenzaldehyde with 25% hydrochloric acid.[2(b)]

Recently, W. M. Schubert, P. Myhre, and A. T. Nielsen[3] observed a colored precipitate in each case when certain 2,4,6-trisubstituted benzaldehydes were heated with mineral acid. They proposed and presented evidence that the red precipitate they obtained was an adduct of one or two moles of aldehyde with one mole of mineral acid. In certain cases they recovered the aldehyde from the complex but did not do so for the product from 2,4,6-trimethoxybenzaldehyde.

Recovery of the aldehyde is, in itself, not conclusive evidence that the product is a simple adduct since similarly substituted diarylcarbinols upon treatment with acid may yield the corresponding triarylmethane and aldehyde in good yield.[2(a,c,e)]

The present work was undertaken to learn the nature of the product and the mode of its formation when 2,4,6-trimethoxybenzaldehyde in greater than $10^{-4}\,M$ concentration was treated with strong hydrochloric acid and perchloric acid.

Two different materials were obtained upon treatment of I with perchloric acid. The first, a light red solid, was obtained if the reaction mixture was cooled a few minutes after mixing. The second, a dark red solid, separated after a longer reaction time. Only the dark red solid could be isolated from the hydrochloric acid experiments.

Since there was no assurance that the first product was pure, no more work was done on it at that time. A planned more extensive study of aldehyde-mineral acid adducts of a number of aromatic aldehydes will include this compound.

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(3) Private communication.