hydrogenation in accordance with previous experience,[1] it was found that the catalyst could be reused and that 18–19 g. could consistently be hydrogenated with 5 g. of catalyst. When a mixture of 10 g. of V, 5 g. of platinum oxide catalyst (J. T. Baker), and 175 cc. of glacial acetic acid was hydrogenated in a Parr apparatus at 30–40 lb., the theoretical quantity of hydrogen was absorbed in three and one-half hours. The catalyst was filtered off and returned to the hydrogenator with 9 g. of V and 175 cc. of acetic acid. After eighteen hours the theoretical quantity of hydrogen had been taken up. The combined acetic acid solutions were worked up as previously described.[1] Crystallization from water gave 17.5 g. (90%) of white solid, m. p. 138–142°.

β-(4-Methoxy-3-nitrobenzoyl)-propionic Acid.—Twenty-five grams of β-(4-methoxybenzoyl)-propionic acid[4] was nitrated with 50 cc. of fuming nitric acid by the procedure used in the preparation of II. Twenty-six grams (85%) of yellow product, m. p. 126–136°, was obtained. After purification through bicarbonate solution with charcoal, crystallization from methanol gave light yellow needles, m. p. 158–159° (softening at 151°).

Anal. Calcd. for $C_{11}H_{11}NO_6$: C, 52.2; H, 4.4; N, 5.5. Found: C, 52.4, 52.3; H, 4.4, 4.5; N, 5.5, 5.6.

The same compound was obtained in low yield from *o*-nitroanisole and succinic anhydride with aluminum chloride in nitrobenzene. This same reaction has been carried out with acetyl chloride by Borsche and Barthenheier.[5]

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[4] Fieser and Hershberg, THIS JOURNAL, **58**, 2314 (1936).

[5] Borsche and Barthenheier, *Ann.*, **553**, 250 (1942).

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1,1-Di-(*p*-chlorophenyl)-ethane

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Need for a small quantity of pure 1,1-di-(*p*-chlorophenyl)-ethane showed that the only preparation reported[1]—the addition of chlorobenzene to acetylene in the presence of aluminum chloride —had given a yellow oil (boiling 210–212° at 30 mm.) having a strong blue fluorescence. The presence of the ethane compound was established by oxidation to 4,4′-dichlorobenzophenone, but the blue fluorescence suggested that impurities of a polycyclic structure were also present.[2]

Several other preparative methods have now been tried, and it is concluded that 1,1-di-(*p*-chlorophenyl)-ethane is best made as follows: (1) di-(*p*-chlorophenyl)-methylcarbinol,[3] prepared from 4,4′-dichlorobenzophenone and methylmagnesium bromide, is (2) dehydrated to 1,1-di-(*p*-chlorophenyl)-ethylene which (3) is hydrogenated to the ethane. Each of these steps proceeds smoothly in good yields: carbinol, 89%; ethylene, 88%; and ethane, 62%.

Pure 1,1-di-(*p*-chlorophenyl)-ethane is a colorless, crystalline solid melting 54–55°. Neither the solid nor its solutions show any fluorescence in visible or ultraviolet light. Oxidation by chromic acid gives almost quantitative yields of 4,4′-dichlorobenzophenone. The melting point of the ethane is noteworthy in that the next lower homolog, di-(*p*-chlorophenyl)-methane, also melts at 55°.[4]

Direct reduction of the di-(*p*-chlorophenyl)-methylcarbinol at 700–800 lb. pressure and 200–205° in the presence of nickel-on-kieselguhr gave only a 14% yield of the ethane. The condensation of acetaldehyde or acetal with chlorobenzene in the presence of aluminum chloride or sulfuric acid gave 38% of a liquid, fluorescent product comparable to that described by Cook and Chambers.[1,5] The Friedel–Crafts reaction of ethylidene chloride and chlorobenzene[2] gave 51% of a liquid product of similar physical properties. Attempts to remove polycyclic impurities from this crude product by selective sulfonation with sulfuric acid or through the formation of addition compounds with picric acid were unsuccessful.

Also tried was the methylation of 4,4′-dichlorobenzohydryl chloride with methylmagnesium bromide. This reaction proceeded almost quantitatively through coupling of the 4,4′-dichlorobenzohydryl groups to form *sym*-tetra-(*p*-chlorophenyl)-ethane. By analogy with the coupling reactions of benzyl halides with methylmagnesium iodide,[6] this reaction probably went as

$$2(p\text{-}ClC_6H_4)_2CHCl + 2CH_3MgBr \longrightarrow (p\text{-}ClC_6H_4)_2CH{-}CH(C_6H_4Cl\text{-}p)_2 + C_2H_6 + 2MgBrCl$$

Experimental

1,1-Di-(*p*-chlorophenyl)-ethane.—Since specific directions for the preparation of the di-(*p*-chlorophenyl)-methylcarbinol and the ethylene derivative are not in the literature,[3] they are given here. In a one-liter three-neck flask fitted with a stirrer, reflux condenser, and dropping funnel was placed 0.25 mole of methylmagnesium bromide in 115 ml. of ether solution. To this was added during forty-five minutes 63 g. (0.25 mole) of 4,4′-dichlorobenzophenone in 700 ml. of dry thiophene-free benzene. A transient purple color developed during the addition of the ketone, possibly because of the intermediate formation of a bromomagnesium ketyl, $(p\text{-}ClC_6H_4)_2COMgBr$.[7] The reaction mixture was then heated to reflux for one hour, cooled, and hydrolyzed by pouring into a mixture of 27 g. of ammonium chloride, 100 ml. of water and 200 g. of ice. After separating the benzene–ether layer, washing with 100 ml. of 2% sodium carbonate solution, then with 100 ml. of water, and drying with Drierite, the solvent was removed by distillation on the steam-bath. The yield of crude product was 59.3 g., 89% of the theoretical, melting 64–68°. Crystallization from 200 ml. of petroleum ether (90–100°) gave 54.2 g., melting 67–68.5°.

Anal. Calcd. for $C_{14}H_{12}OCl_2$: Cl, 26.58; mol. wt., 267. Found: Cl, 26.62; mol. wt., 266.

The melting point of 167–168° previously reported for this compound is probably the result of a typographical error.[3]

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[1] Cook and Chambers, THIS JOURNAL, **43**, 334 (1921).

[2] A further reason for suspecting that such impurities were present was the fact that anthracene derivatives have been found along with 1,1-diphenylethane from a closely-related reaction, the Friedel–Crafts reaction of benzene and ethylidene chloride, by Anschütz *et al.*, *Ber.*, **17**, 165 (1884); **18**, 662 (1885); *Ann.*, **235**, 302 (1886).

[3] Bergmann and Bondi, *Ber.*, **64B**, 1455 (1931).

[4] Montagne, *Rec. trav. chim.*, **25**, 379 (1906).

[5] Bodendorf used the acetaldehyde–chlorobenzene–aluminum chloride reaction for the preparation of 1,1-diphenylethane; *J. prakt. Chem.*, **129**, 337 (1931).

[6] Späth, *Monatsh.*, **34**, 1965 (1913); Fuson, THIS JOURNAL, **48**, 2681 (1926).

[7] Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

The carbinol was dehydrated by heating 10 g. (0.037 mole) under reflux in an oil-bath at 210–215° for fifteen minutes, cooling, adding 10 ml. of 20% sulfuric acid, refluxing one hour, and again cooling. Suction filtration of the crude product and crystallization from 85 ml. of 95% alcohol (with Norit) gave 8.1 g., 88%, melting 84–86°.[3]

A mixture of 5 g. (0.02 mole) of 1,1-di-(*p*-chlorophenyl)-ethylene, 80 ml. of absolute alcohol, and 0.15 g. of Adams platinum black catalyst was allowed to react with hydrogen at 35 pounds pressure in the Parr low-pressure hydrogenator for thirty minutes. The pressure drop corresponded to 0.02–0.03 mole of hydrogen consumed. After filtering and removal of the solvent the residue was crystallized from 90% acetic acid to give 3.1 g., 62% of the theoretical, melting 54–55°, boiling 143–145° at 1–2 mm. pressure. Neither the pure product nor its solutions showed any fluorescence in visible or ultraviolet light.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: Cl, 28.24; mol. wt., 251. Found: Cl, 28.18; mol. wt., 252.

When the time of hydrogenation was two hours, considerably more than the theoretical amount of hydrogen was consumed, the reaction mixture contained dissolved hydrogen chloride, and the yield of ethane was only 0.7 g. (14%). Apparently some hydrogenolysis of the chlorine atoms occurred.

Oxidation of 1.0 g. of the ethane by a solution of 40 ml. of glacial acetic acid containing 4 g. of chromic acid and four drops of sulfuric acid at reflux for two hours gave 0.9 g. of 4,4′-dichlorobenzophenone, melting 142–144°, which showed no depression in a mixed melting point with the authentic ketone. A mixed melting point of the ethane with authentic di-(*p*-chlorophenyl)-methane[4] (m. p. 54–55°) was 40–50°. A picrate derivative of the ethane did not form from the usual procedure.[8]

Reduction of Di-(*p*-chlorophenyl)-methylcarbinol.—A mixture of 13.4 g. (0.05 mole) of carbinol, 40 ml. of absolute alcohol and about 3 g. of nickel-on-kieselguhr (prepared from Harshaw Chemical Co. no. 78 catalyst, nickel carbonate on kieselguhr) was hydrogenated in an American Instrument high-pressure hydrogenator at 200–205° for 3.5 hours. The initial pressure at room temperature was 710 pounds, and the pressure drop of 540 pounds represented 0.1 mole of hydrogen. Isolation of the product as described before gave 1.8 g. of ethane, 14%, melting 54–55°. Undoubtedly this yield could be increased by further study of the hydrogenation conditions.

Acetaldehyde plus Chlorobenzene.—Eighty grams (0.6 mole) of anhydrous aluminum chloride was added to 150 ml. of chlorobenzene and the mixture saturated at 0° with anhydrous hydrogen chloride. Twenty-two grams (0.5 mole) of acetaldehyde dissolved in 50 ml. of chlorobenzene was added dropwise and with stirring during one hour, the temperature being held at 0–10° by an ice-bath. The reaction was continued for four hours at 50°, the product hydrolyzed in cold dilute hydrochloric acid and then steam distilled to remove excess chlorobenzene. The residue was dried and distilled to give 25 g. (20% yield calculated as di-(*p*-chlorophenyl)-ethane) at 160–170° and 6–7 mm. pressure. Redistillation gave 22 g., 167–168° (6–7 mm.) of a yellow oil showing a strong blue fluorescence; n^{20}_{D} 1.5918. Oxidation with chromic acid in acetic acid gave 4,4′-dichlorobenzophenone, m. p. 143–144°. Analysis showed that the chlorine content was slightly lower than that for di-(*p*-chlorophenyl)-ethane.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: Cl, 28.24. Found: Cl, 28.04, 28.05.

The substitution of 15% fuming sulfuric acid for aluminum chloride in a similar experiment gave only black, tarry products; 7.5 g. (0.17 mole) of acetaldehyde, 59.8 g. (0.53 mole) of chlorobenzene and 89 ml. of 15% fuming sulfuric acid were taken. In a final experiment acetal instead of acetaldehyde was used, but again the only product was a black resinous mass; 20 g. (0.17 mole) of acetal, 59.8 g. (0.53 mole) of chlorobenzene, and 89 ml. of 15% fuming sulfuric acid were taken.

Ethylidene Chloride plus Chlorobenzene.—To a mixture of 316.8 g. (2.8 mole) of chlorobenzene and 39.9 g. (0.3 mole) of aluminum chloride in a 500-ml. three-neck flask was added dropwise 59.4 g. (0.6 mole) of ethylidene chloride during one hour. The reaction was stirred and cooled in an ice-bath to 0–10°. After an additional one-half hour the mixture was hydrolyzed with 200 g. of ice and 75 ml. of concentrated hydrochloric acid. After washing and drying the product was distilled at 162–166° (6 mm.) to give 77 g. (51%) of a yellow, blue-fluorescent oil; n^{20}_{D} 1.5961. A resinous distillation residue of 21 g. was also strongly fluorescent. Oxidation to the ketone and analysis for chlorine indicated that 1,1-di-(*p*-chlorophenyl)-ethane was present.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: Cl, 28.24. Found: Cl, 28.27, 28.30.

The attempted purifications with sulfuric acid and picric acid were as follows: 72 g. of the crude ethane and an equal volume of 80% sulfuric acid were stirred at room temperature for ten hours. The acid layer was discarded, fresh acid added and the treatment continued for twelve hours. After washing, drying, and distilling there was obtained 53.5 g. at 162–163° (6 mm.), n^{20}_{D} 1.5942, and a distillation residue of 15 g. The fluorescence was still apparent but less intense than that of the original. A mixture of 15 g. of this material, 10 g. of picric acid and 100 ml. of alcohol was refluxed one hour, cooled, and filtered. After washing and drying the filtrate it was distilled at 156–157° (4 mm.); n^{20}_{D} 1.5947. The distilled oil showed no decrease in fluorescence and did not crystallize at 0–10°.

4,4′-Dichlorobenzohydryl Chloride plus Methylmagnesium Bromide.—To 30 g. (0.11 mole) of the chloride (m. p. 58–60°)[9] in 200 ml. of dry ether was slowly added 50 ml. of 2.40 *N* methylmagnesium bromide (0.12 mole) at 0–10°. No reaction appeared to take place but on allowing the mixture to come to room temperature the ether refluxed vigorously and a white granular precipitate formed. After hydrolysis with 200 g. of ice, 200 ml. of water, and 20 g. of ammonium chloride, a white precipitate formed. Evaporation of the ether layer gave 2 g. of an oily low-melting solid which appeared to be mostly the original chloride. The insoluble product consisted of 24.8 g. which in a melting point determination started to decompose at about 300°, turned dark red and appeared to evolve gas at 327–328°. Crystallization from nitrobenzene did not alter the melting point behavior, which corresponds to that described for *sym*-tetra-(*p*-chlorophenyl)-ethane.[9] The yield of ethane calculated on the chloride taken was 95%. A second experiment in which the order of addition of the reactants was reversed gave the same result.

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[8] Shriner and Fuson, "Identification of Organic Compounds," second edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 149.

[9] Montagne, *Rec. trav. chim.*, **25**, 394 (1906).

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Chemical Nature of the Insecticidal Principle in Mamey Seed

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On account of the scarcity of plant insecticides, such as pyrethrum and rotenone, considerable interest has centered in the possible value of other sources, especially those plants already established in the western hemisphere. Among such plants is the mamey tree (*Mammea americana* L.) various parts of which have been used and some found to be highly toxic to certain insects.[1] The

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[1] H. K. Plank, *J. Econ. Entomol.*, **37** (6), 737–739 (1944).