91–117°, mixture A. The aqueous filtrate from which A separated was combined with the aqueous part of the original hydrolysis mixture. This solution contained the water-soluble acids, mixture B.

Mixture A was separated by steam distillation. Benzoic acid, 0.04 g., m.p. 122–123°, was isolated from the distillate. The m.p. of a mixture with authentic benzoic acid was not depressed. γ-Benzoylbutyric acid, 0.80 g., m.p. 124.5–127.5°, was isolated from the distilland. After one recrystallization from water, the acid had m.p. 127.5–128.5°. The m.p. of a mixture with authentic γ-benzoylbutyric acid of m.p. 128.5–129.5° was not depressed; reported melting points of γ-benzoylbutyric acid are 127.5°[8] and 132°.[9] The semicarbazone had m.p. 211.5–212° dec. after one recrystallization from water, reported m.p. 213° dec.[9]

Mixture B was separated by steam distillation. Acetic acid (0.2 g. by titration) was identified in the distillate by preparing its *p*-bromophenacyl ester, m.p. 83–84.5°; the reported m.p. of *p*-bromophenacyl acetate is 85°.[10] Extraction of the distilland with ether gave, after drying and removing the ether, 0.39 g. of crude γ-acetylbutyric acid. The semicarbazone had m.p. 173–173.5° dec. The reported m.p. of γ-acetylbutyric acid semicarbazone is 173–174° dec.[7]; the m.p. of a mixture with authentic semicarbazone was not depressed.

Hydrolysis of III.—When III was refluxed with aqueous hydrochloric acid a 68% yield of crude γ-acetylbutyric acid containing acetic acid (odor) was obtained. The semicarbazone melted at 173.5° dec.; reported m.p. of γ-acetylbutyric acid semicarbazone is 173–174° dec.[7] The melting point of a mixture with authentic γ-acetylbutyric acid semicarbazone was not depressed.

Hydrolysis of IV.—Refluxing IV with aqueous hydrochloric acid gave a mixture of benzoic acid, m.p. 122–123°, and γ-benzoylbutyric acid, m.p. 128.5–129.5°; reported melting points of γ-benzoylbutyric acid are 127.5°[8] and 132°.[9] The melting point of a mixture of the benzoic acid from the hydrolysis of IV and authentic benzoic acid was not depressed. The semicarbazone of the γ-benzoylbutyric acid had m.p. 210–210.5° dec. The reported m.p. of γ-benzoylbutyric acid semicarbazone is 213° dec.[9]

Hydrolysis of VI.—Refluxing VI with aqueous hydrochloric acid gave a 94.3% yield of crude γ-benzoylbutyric acid. One recrystallization from water gave a 68.6% yield of γ-benzoylbutyric acid, m.p. 128.5–129.5°; reported melting points 127.5°[8] and 132°.[9] The melting point of a mixture with authentic γ-benzoylbutyric acid was not depressed.

BRECKSVILLE, OHIO

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[8] J. Wislicenus and C. K. Kuhn, *Ann.*, **302**, 219 (1898).

[9] A. Ali, *et al.*, *J. Chem. Soc.*, 1013 (1937).

[10] "The Systematic Identification of Organic Compounds," R. L. Shriner and R. C. Fuson, 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 222.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, DOMINION TAR & CHEMICAL CO.]

Studies in Chlorination of Diarylethanes. New Synthesis of DDT Analogs

BY HENRY BADER,[1] W. A. EDMISTON AND H. H. ROSEN

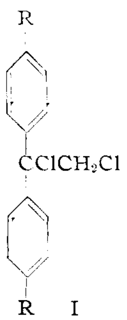
RECEIVED NOVEMBER 25, 1955

Direct chlorination of 1,1-diarylethanes led to analogs of DDT, all having chlorine substituted in the 1-position of the ethylidene group. Sulfuryl chloride in presence of benzoyl peroxide gave the 1,2-dichloro-1,1-diarylethanes (I, R = Cl and Me). Chlorine in presence of peroxides yielded 1,2,2-trichloro-1,1-ditolylethane and 1,2,2,2-tetrachloro-1,1-di-(*p*-chlorophenyl)-ethane. Good yields of highly ring-chlorinated diarylethanes were obtained with chlorine in the presence of ferric chloride or iron dust.

Though a very large number of analogs of DDT have been prepared, the main emphasis was on substitution in the aromatic rings or on variation in the number of chlorine atoms in the aliphatic side-chain and their replacement by isosteric groups. No compounds seem to have been evaluated bearing a chlorine atom in the position 1 of the aliphatic chain, with the exception of the *p*,*p*'-substituted 1,2,2,2-tetrachloro-1,1-diphenylethanes,[2] prepared by chlorination of the corresponding 2,2,2-trichloroethanes or of the 2,2-dichloroethylenes. A recent review by Gunther and Blinn[3] demonstrates as well the usefulness of DDT-type compounds in organic synthesis. An additional point of interest in the 1-chloro derivatives is that they could be expected to form by direct chlorination of the corresponding unsymmetrical diarylethanes.

Some controversial data have been reported on the side-chain chlorination of diphenylethane. According to Sheibley and Prutton[4] 2,2-dichloro-1,1-diphenylethylene is the main product of direct chlorination at 100–150° in the presence of sunlight. Li,[5] on the other hand, reported the successive formation of a monochloro derivative at 10°, of 1,2,2-trichloro-1,1-diphenylethane between 10–160° and of 1,2,2,2-tetrachloro-1,1-diphenylethane between 160–180°. Some ring chlorination also occurred yielding 1,2,2-trichloro-1,1-phenyl-(*x*-chlorophenyl)-ethane and 2,2-dichloro-1,1-phenyl-(*x*-chlorophenyl)-ethylene. Finally a Japanese patent[6] claimed to prepare a mixture of 1,2,2,2-tetrachloro-1,1-diphenylethane and 1,2,2-trichloro-1,1-diphenylethane by passing chlorine into diphenylethane in sunlight. No chlorination of diaryl ethanes other than diphenylethane seems to have been reported in the literature.

The aim of the present work was to apply the direct chlorination of diarylethanes to the prepara-



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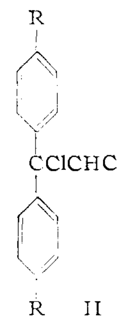

II

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[1] Ortho Research Foundation, Raritan, N. J.

[2] I. E. Balaban, British Patent 632,639 (1949).

[3] F. A. Gunther and R. C. Blinn, *J. Chem. Education*, **27**, 654 (1950).

[4] F. E. Sheibley and C. F. Prutton, THIS JOURNAL, **62**, 840 (1940).

[5] H. Y. Li, *J. Chem. Soc. Japan*, **64**, 1399 (1943); *C. A.*, **41**, 3779 (1947).

[6] S. Kubota and A. Nkamur, Japanese Patent 175,484 (1948); *C. A.*, 44, 8046 (1950).

tion of compounds substituted in both positions 1 and 2 of the ethylidene side-chain, such as shown by the structures I and II.

The diarylethanes chosen were 1,1-di-(*p*-tolyl)-ethane (containing 10% of the *o,p'*- and 90% of the *p,p'*-isomers and prepared by the Fischer method as improved by McCoubrey[7]) and 1,1-di-(*p*-chlorophenyl)-ethane, prepared by an improved synthesis from chlorobenzene and ethylidene diacetate in presence of a mixture of fluorosulfonic acid and hydrogen fluoride.[8]

It would have been expected that by varying the chlorinating agents rather than the conditions of chlorination one might be able to find selective methods of preparation of both types I and II of the desired compounds. This was found to be the case when alternatively sulfuryl chloride or chlorine were used at the appropriate temperatures. Benzoyl peroxide was employed instead of ultraviolet radiation as a source of free radicals as it gave more reproducible results.

Thus 1,1-di-(*p*-tolyl)-ethane and sulfuryl chloride reacted at reflux temperature in presence of catalytic amounts of benzoyl peroxide to give 1,2-dichloro-1,1-di-(*p*-tolyl)-ethane (I, R = Me) in good yield, together with an almost complete recovery of the unreacted starting material. The product failed to hydrolyze after heating at 100° for 3 hr. with water or even with a 15% solution of potassium hydroxide, which indicated that the chlorine was not present in the *p,p'*-methyl groups. Depression of its melting point by 2,2-dichloro-1,1-di-(*p*-tolyl)-ethane eliminated the possibility of this isomeric structure. A complete ring chlorination of this compound produced a decachloro derivative V further confirming the structure I (R = Me).

When 1,2-dichloro-1,1-di-(*p*-tolyl)-ethane was heated with sodium 2-ethylhexoxide in 2-ethylhexanol or better with metallic sodium in xylene, the *p,p'*-dimethyltolane was obtained. Similar Wagner rearrangements by dehydrohalogenation in the 1,1-diarylethane series were previously reported by Buttenberg[9] who obtained *p,p'*-dimethyltolane from 2-chloro-1,1-di-(*p*-tolyl)-ethylene and sodium ethoxide.

Chlorination of 1,1-di-(*p*-chlorophenyl)-ethane in a similar manner gave the corresponding 1,2-dichloro-1,1-di-(*p*-chlorophenyl)-ethane (I, R = Cl) which was proved by mixed melting points to be different from the isomeric 2,2-dichloro-1,1-di-(*p*-chlorophenyl)-ethane ("DDD").

The above results are of a special interest in view of the inertness of diphenylmethane to a peroxide-catalyzed chlorination with sulfuryl chloride, as reported by Kharasch and Brown.[10]

Chlorination with sulfuryl chloride never proceeded beyond the stage of substitution of two chlorine atoms. In order to introduce a third chlorine atom, chlorine was added to the diarylethane in presence of catalytic amounts of benzoyl peroxide. The temperature of the reaction mixture was kept at 120°, but it was found that substitution of the fourth chlorine in the ethylidene side-chain did not occur below 160° when the starting material was 1,1-di-(*p*-tolyl)-ethane. In this way 1,2,2-trichloro-1,1-di-(*p*-tolyl)-ethane (II, R = Me) was prepared in a yield of 60%. The structure assigned was confirmed by depression of melting points on admixture with 2,2,2-trichloro-1,1-di-(*p*-tolyl)-ethane. When the ditolyl compound II (R = Me) was refluxed with ethanolic potassium hydroxide, it dehydrochlorinated to 2,2-dichloro-1,1-di-(*p*-tolyl)-ethylene identical with the product of dehydrochlorination of the isomeric 2,2,2-trichloro-1,1-di-(*p*-tolyl)-ethane under the same conditions.[11] Although the chlorination of 1,1-di-(*p*-tolyl)-ethane could be stopped easily at the stage of addition of three chlorine atoms, in the case of 1,1-di-(*p*-chlorophenyl)-ethane this was not possible. The chlorination of this latter compound was carried out several times, but in every case the chlorination proceeded quickly to the stage of the known 1,2,2,2-tetrachloro-1,1-di-(*p*-chlorophenyl)-ethane.

The results of direct chlorination indicate that 1,1-di-*p*-tolylethane gives rise to similar products as does diphenylethane at the corresponding temperature ranges, at least as reported by the Japanese workers.[5,6] No evidence was found of 2,2-dichloro-1,1-diarylethanes, analogous to the rather controversial 2,2-dichloro-1,1-diphenylethylene, reported by Sheibley and Prutton (the structure of which seems not to be convincingly established). Chlorination of 1,1-di-(*p*-chlorophenyl)-ethane is much easier than that of diphenyl- or ditolylethane, both in rate and in extent of side-chain chlorination under comparable conditions.

In addition, the preparation of ring chlorinated derivatives of 1,1-ditolylethane with a high chlorine content was carried out for testing both as insecticides and as fire retarding plasticizers. The method used was to add gaseous chlorine at atmospheric pressure to the solution of the diarylethane in chloroform or carbon tetrachloride in presence of iron dust or ferric chloride as catalyst. The temperature of the reaction mixture was kept below 40° by external cooling. The degree of chlorination was controlled by the weight of chlorine added or by observing changes in viscosity of the mixture. Addition of solvents was found necessary in order to reduce the viscosity of the reaction mixture in the late stages of chlorination and in order to prevent a crystallization of intermediate products before the end of the reaction.

When 1,1-di-(*p*-tolyl)-ethane was chlorinated in this manner, the reaction could be stopped at the stage of 1,1-di-(trichloro-*p*-tolyl)-ethane (III) (50% yield of isolated product). Further chlorination yielded 1,1-di-(tetrachloro-*p*-tolyl)-ethane (IV), which then split by addition of another chlorine molecule to give pentachlorotoluene. This process started before all the hexachloro derivative (III) disappeared and it was noticeable by a marked decrease in viscosity of the mixture. When the reaction was stopped at the moment the viscosity of the mixture started falling, the octachloro deriva-

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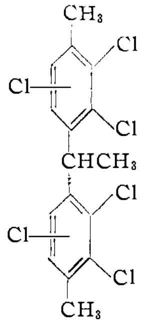
(7) J. A. McCoubrey, Canadian Patent 468,405 (1950); J. A. McCoubrey and F. P. Lossing, U. S. Patent 2,500,369 (1950); J. K. Dixon and K. W. Saunders, *Ind. Eng. Chem.*, **46**, 652 (1954).

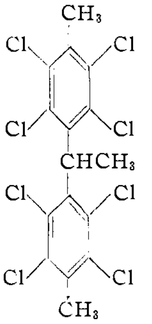
(8) H. Bader and W. A. Edmiston, *Can. J. Chem.*, **34**, 383 (1956).

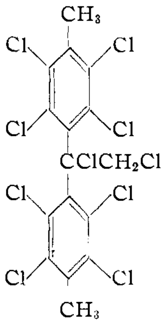
(9) W. P. Buttenberg, *Ann.*, **273**, 335 (1893).

(10) M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

(11) O. Fischer, *Ber.*, **7**, 1191 (1874).


III


IV


V

tive IV was obtained in a similar yield. The fission of alkyl substituents by chlorination is analogous to the splitting of the isopropyl chain on ring-chlorination of cumene and of *p*-cymene.[12]

The ring chlorination was repeated under similar conditions with 1,2-dichloro-1,1-di-(*p*-tolyl)-ethane (I, R = Me), but here the fully ring-chlorinated decachloro compound V did not split to pentachlorotoluene on further chlorination, and could be isolated in good yield. It would seem that the chlorine in the 1-position of the ethylidene side-chain has a stabilizing effect on the diarylethane structure. This probably results from the electron deficiency created on the ring carbon atom, to which the chain is attached, by the electron-attracting chlorine in the side-chain. This ring carbon atom thus has less chance to be attacked by positive chlorine ions. It has, therefore, also less chance of forming a carbonium ion which would cause a rupture of a carbon–carbon bond.

Comparison of compounds IV and V, both obtained under similar conditions of ring-chlorination, further confirmed the structure of the dichloro compound I (R = Me) as containing no ring-substituted chlorine.

Experimental[13,14]

1,2-Dichloro-1,1-di-(*p*-tolyl)-ethane (I, R = Me).—A mixture of 1,1-di-(*p*-tolyl)-ethane[7] (546 g.) and of sulfuryl chloride (1106 g.) was refluxed for a period of 12 hr., solid benzoyl peroxide (28 g. in all) being added in small portions at the beginning of each hour. At the end of the reaction the evolution of hydrogen chloride ceased. The excess of benzoyl peroxide was destroyed by adding 60 cc. of a saturated alcoholic solution of stannous chloride and refluxing for another hour. Ether was then added and the solution washed with a 10% solution of sodium hydroxide, and then with water and saturated brine. The extract was dried, solvent removed by distillation and the residue fractionated. The partly-solidified distillate was crystallized from ethanol, the mother liquors purified by further distillation and crystallizations yielding altogether 209.3 g. (38.2%) of recovered ditolylethane and 380.5 g. (54.5%) of 1,2-dichloro-1,1-di-(*p*-tolyl)-ethane, b.p. 125–126° (0.01 mm.), crystallized in long colorless needles, m.p. 91–95° (from ethanol), depressed on admixture with a sample of 2,2-dichloro-1,1-di-(*p*-tolyl)-ethane, m.p. 80°.[15]

Anal. Calcd. for $C_{16}H_{16}Cl_2$: C, 68.8; H, 5.75; Cl, 25.4. Found: C, 68.8; H, 5.55; Cl, 25.45.

The isothiouronium picrate was obtained as yellow needles, m.p. 166–171° (from ethanol).

4,4'-Dimethyltolane.—(1) Sodium (2.07 g.) was dissolved in 2-ethylhexanol (150 cc.), 1,2-dichloro-1,1-di-(*p*-tolyl)-ethane (11.2 g.) and potassium iodide (0.5 g.) were then added and the solution refluxed for 24 hr. Ether and water were added, the aqueous layer extracted with ether and the extract dried. Removal of solvent and distillation of the excess of 2-ethylhexanol left a residue which was dissolved in petroleum ether (boiling range 30–60°) and adsorbed on an alumina column (2.7 × 75 cm.). Elution with petroleum ether (1250 cc.) yielded, after evaporation of the solvent, the starting material (8.5 g., 76%). Further elution with a 1:3 benzene–petroleum mixture (600 cc.) gave 4,4'-dimethyltolane (2.0 g., 24.0%), which after 3 crystallizations from petroleum ether (boiling range 30–60°) formed colorless plates, m.p. 134–136° (reported[16] 136°).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.15; H, 6.85; mol. wt., 206.3. Found: C, 92.95; H, 6.95; av. mol. wt., 210.3.

(2) Sodium (5.6 g.) and 1,2-dichloro-1,1-di-(*p*-tolyl)-ethane (10.0 g.) were heated in refluxing xylene (200 cc.) for 9 hr., the liquid layer decanted and the residue extracted with more xylene. After the removal of solvent, the residue was distilled and gave crude 4,4'-dimethyltolane (2.59 g., 61.8%), b.p. 130–145° (0.2 mm.), m.p. 118–134°. The sample, purified by crystallization from petroleum-ether (boiling range 30–60°) had m.p. 134–136° identical with this prepared by method 1 (m.m.p.).

1,2-Dichloro-1,1-di-(*p*-chlorophenyl)-ethane (I, R = Cl).—Sulfuryl chloride (90.0 g.) and benzoyl peroxide (2.0 g.) were added periodically in small portions to 50.4 g. of 1,1-di-(*p*-chlorophenyl)-ethane[8] while the mixture was being refluxed. After 6 hr., 10 cc. of a saturated alcoholic solution of stannous chloride was added and the mixture refluxed for a further 20 minutes in order to destroy the excess of peroxide. The excess of ethanol was then distilled and the residue extracted 4 times with ether, the extracts washed with water, dried with anhydrous calcium sulfate and the solvent removed by distillation. Fractional distillation of the residue gave the recovered 1,1-di-(*p*-chlorophenyl)-ethane (25.6 g., 51.0%) and an oil (25.0 g.) boiling at 165–171° (0.5 mm.). The latter was dissolved in 25 parts of petroleum ether (b.p. 30–60°) and the solution adsorbed on an alumina column (3.5 × 60 cm.). Elution with 6000 cc. of petroleum ether (b.p. 30–60°) and removal of the solvent by distillation left a residue (21.1 g.), which was crystallized from methanol to give 1,2-dichloro-1,1-di-(*p*-chlorophenyl)-ethane (11.7 g., 18.0%), crystallized in colorless plates, m.p. 87.8–88.5°, depressed on admixture with a sample of 2,2-dichloro-1,1-di-(*p*-chlorophenyl)-ethane, m.p. 110°.[17]

Anal. Calcd. for $C_{14}H_{10}Cl_4$: C, 52.55; H, 3.1; Cl, 44.35. Found: C, 52.5; H, 2.6; Cl, 44.15.

1,2,2-Trichloro-1,1-di-(*p*-tolyl)-ethane (II, R = Me).—Gaseous chlorine was passed through a well-stirred mixture of 1,1-di-(*p*-tolyl)-ethane (52.5 g.) and benzoyl peroxide (1.25 g.) kept at 120° for 3.5 hr., by which time the increase of weight of the mixture corresponded to 3.09 chlorine atoms per mole of the hydrocarbon (26.6 g.). A saturated alcoholic solution (15 cc.) of stannous chloride was added and the stirring continued for another 15 minutes. Potassium hydroxide solution (25 cc., 10%) was then added and the mixture extracted with ether. Washing of the extract with water, drying over calcium chloride and removal of solvent left a residue which was fractionally distilled yielding 1,2,2-trichloro-1,1-di-(*p*-tolyl)-ethane (47.0 g., 60.0%), as a yellow oil, b.p. 175–180° (0.7 mm.), $n^{21}D$ 1.6159 which gave colorless plates (29.8 g., 37.0%), m.p. 85.0–87.5°, after five crystallizations from ethanol. Admixture of a sample of 2,2,2-trichloro-1,1-di-(*p*-tolyl)-ethane, m.p. 89°,[11,18] depressed the melting point.

Anal. Calcd. for $C_{16}H_{15}Cl_3$: Cl, 33.9. Found: Cl, 34.3.

2,2-Dichloro-1,1-di-(*p*-tolyl)-ethylene.—1,2,2-Trichloro-1,1-di-(*p*-tolyl)-ethane (2.5 g.) and potassium hydroxide (1.7 g.) were refluxed in dry ethanol (75 cc.) for 21 hr. The solution was neutralized with dilute hydrochloric acid, evaporated to dryness under reduced pressure, then water was added and the organic material extracted with ether. Removal of the solvent from the dried extract gave an oil which crystallized from ethanol to give 2,2-dichloro-1,1-di-(*p*-tolyl)-ethylene (1.3 g., 58.8%) as colorless needles, m.p. 91–92°,

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[12] W. Quist and N. Holmberg, *Acta Acad. Aboensis Math. Phys.*, **6**, No. 14, 3 (1932); *C. A.*, **27**, 5726 (1933); W. Quist and A. Salo, *ibid.*, **8**, No. 4, 30 (1934); *C. A.*, **29**, 6884 (1935).

[13] All melting points are uncorrected.

[14] Microanalyses by Dr. Rob. Dietrich, Zurich, Switzerland.

[15] W. P. Buttenberg, *Ann.*, **279**, 334 (1894).

[16] G. Goldschmiedt and E. Hepp, *Ber.*, **6**, 1505 (1873).

[17] J. Forrest, O. Stephenson and W. A. Waters, *J. Chem. Soc.*, 333 (1946).

[18] L. Haskelberg and D. Lavie, *J. Org. Chem.*, **14**, 501 (1949).

undepressed on admixture with a sample prepared by dehydrohalogenation of 2,2,2-trichloro-1,1-di-(*p*-tolyl)-ethane.[11]

Anal. Calcd. for $C_{16}H_{14}Cl_2$: C, 69.3; H, 5.1; Cl, 25.6. Found: C, 69.4; H, 5.2; Cl, 25.45.

1,2,2,2-Tetrachloro-1,1-di-(*p*-chlorophenyl)-ethane.—Gaseous chlorine was passed through a well-stirred mixture of 1,1-di-(*p*-chlorophenyl)-ethane (20.0 g.) and benzoyl peroxide (0.3 g.) at 120° during a period of 5.5 hr. by which time the take-up of chlorine ceased. Ethanol (125 cc.) was then added to the reaction mixture and on standing 1,2,2,2-tetrachloro-1,1-di-(*p*-chlorophenyl)-ethane (26.5 g., 86.5%) crystallized in colorless rhombohedric prisms, m.p. 91–92°.[19]

Anal. Calcd. for $C_{14}H_8Cl_6$: Cl, 54.76. Found: Cl, 54.05.

Although several attempts were made to stop the reaction at an earlier stage of chlorination, no 1,2,2-trichloro-1,1-di-(*p*-chlorophenyl)-ethane could be isolated.

1,1-Di-(tetrachloro-*p*-tolyl)-ethane (IV).[20]—Chlorine gas was passed through a solution of 1,1-di-(*p*-tolyl)-ethane (50.0 g.) in carbon tetrachloride (100 cc.) containing iron dust (5 g.) and kept at 25° by external cooling, for a period of 5 hr. until 81 g. of chlorine was absorbed. By this time the original thickening of the solution had stopped and the thinning just started. Making allowance for the formation of ferric chloride, about 71 g. of chlorine was absorbed by the diarylethane. The reaction mixture was filtered hot from the inorganic residue, the solvent removed under reduced pressure and the residue extracted with hot benzene leaving behind 1,1-di-(tetrachloro-*p*-tolyl)-ethane (60.3 g., 52%) as colorless prisms, m.p. 231–236°, which after recrystallization from benzene melted at 234–236° (30.9 g., 26.6%).

Anal. Calcd. for $C_{16}H_{10}Cl_8$: C, 39.55; H, 2.05; Cl, 58.4. Found: C, 39.7; H, 2.05; Cl, 58.35.

Steam distillation of the benzene extract yielded pentachlorotoluene (12.5 g.), m.p. 224°.[12]

Anal. Calcd. for $C_7H_3Cl_5$: C, 31.8; H, 1.15; Cl, 67.0. Found: C, 32.2; H, 1.4; Cl, 66.5.

1,1-Di-(trichloro-*p*-tolyl)-ethane (III).[20]—The conditions of the reaction differed from those of the above experiment in that the addition of chlorine was interrupted after 3.5 hr., when only 55 g. was absorbed. Benzene was added to the reaction mixture and the solution so obtained was filtered, washed with water and evaporated to dryness. Crystallization of the residue from petroleum ether (boiling range 65–110°) gave an isomeric mixture of 1,1-di-(trichloro-*p*-tolyl)-ethane (49.3 g., 50%) as colorless rosettes of needles, m.p. 179–189°.

Anal. Calcd. for $C_{16}H_{12}Cl_6$: C, 46.1; H, 2.9; Cl, 51.05. Found: C, 45.6; H, 2.75; Cl, 51.6.

1,2-Dichloro-1,1-di-(tetrachloro-*p*-tolyl)-ethane (V).—Chlorine gas was passed through a solution of 1,2-dichloro-2,2-di-(*p*-tolyl)-ethane (25.0 g.) in carbon tetrachloride (50 cc.) containing iron powder (1 g.) and kept at 25–35° by external cooling. After 14 hr. of addition, when 26 g. of chlorine was absorbed (*i.e.*, 24 g. absorbed by the diarylethene) the weight of the mixture remained constant. The solvent was removed under pressure and the residue redissolved in 600 cc. of hot benzene. This solution was washed 3 times with water in order to remove ferric chloride and then concentrated and cooled yielding 1,2-dichloro-1,1-di-(tetrachloro-*p*-tolyl)-ethane (32.4 g., 65%), m.p. 223–225°, which crystallized from benzene in colorless prisms, m.p. 226–227° (21.6 g., 43.3%).

Anal. Calcd. for $C_{16}H_8Cl_{10}$: C, 34.65; H, 1.45; Cl, 63.9. Found: C, 35.0; H, 1.25; Cl, 63.75.

VILLE LASALLE, QUEBEC, CANADA

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[19] O. Grummitt, A. Buck and A. Jenkins, THIS JOURNAL, **67**, 155 (1945), also give 91–92°.

[20] With the collaboration of Mr. M. A. Davis.

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Aromatic Fluorine Compounds. VI. Displacement of Aryl Fluorine in Diazonium Salts[1,2]

BY G. C. FINGER AND R. E. OESTERLING

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Several chlorofluorobenzenes have been isolated from the Schiemann synthesis of fluorobenzenes. These have been shown to be the products of two side reactions occurring during thermal decomposition of the dry benzenediazonium fluoborate salt containing coprecipitated sodium chloride, an unavoidable contaminant in large preparations involving the use of hydrochloric acid and sodium fluoborate. The major side reaction and its chloro product were unexpected; a unique displacement of fluorine *ortho* to the diazonium group was observed. Replacement of the diazo group with chlorine was the predicted side reaction which proved to be minor. Conditions causing the side reactions and the isolation and identification of the products are described.

Discussion

Diazotization for the Schiemann synthesis is usually effected in hydrochloric acid, and sodium fluoborate is the most convenient source of the fluoborate ion. If the precipitated diazonium fluoborate is dried as such, it contains varying amounts of coprecipitated sodium chloride, which may affect the final thermal decomposition reaction. Recrystallization of the benzenediazonium fluoborate is impractical for large-scale syntheses, and organic solvents are ineffective in removing sodium chloride. As a result, appreciable amounts of chlorobenzenes[3] may be formed in the preparation of some fluorobenzenes. The chloro mixtures from three such preparations have been isolated and identified.

A 10% yield of 2,5-difluorochlorobenzene (IV) and 1% of 2,4-difluorochlorobenzene (V) in the synthesis of 1,2,4-trifluorobenzene (II)[4] from 2,4-difluoroaniline was the first observed instance of the formation of two chloro isomers. The identical isomers were also obtained from 2,5-difluoroaniline with 2,4-difluorochlorobenzene as the major component. 2,4,6-Trifluorochlorobenzene with a trace of 2,3,5-trifluorochlorobenzene was obtained in the synthesis of 1,2,3,5-tetrafluorobenzene[5] from 2,3,5-trifluoroaniline. These compounds gave evidence

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[2] Published with the permission of the Chief of the Illinois State Geological Survey.

[3] G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort and R. R. Blough, THIS JOURNAL, **73**, 145 (1951). The assistance of Messrs. R. H. White and R. H. Shiley in providing residues from large scale Schiemann syntheses is kindly acknowledged.

[4] G. Schiemann, *J. prakt. Chem.*, **140**, 97 (1934).

[5] G. C. Finger, F. H. Reed and R. E. Oesterling, THIS JOURNAL, **73**, 152 (1951).