investigation, and to L. M. White and Geraldine Secor for performing the microanalyses.

Summary

Alkyl ethers of *p*-hydroxydiphenylamine have been prepared from a variety of alkyl halides and have properties suitable for use in identification of alkyl halides. Ether formation from primary halides was general, but secondary alkyl halides did not always operate satisfactorily. Tertiary halides were not investigated.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

Pentachlorophenyl Derivatives. III. The Effect of Temperature on the Composition of the Product in the Chlorination of Ethylpentachlorobenzene

BY SIDNEY D. ROSS, MOUSHY MARKARIAN AND MATTHEW NAZZEWSKI

In previous reports from this Laboratory[1] it was shown that the major product isolated from the chlorination of ethylpentachlorobenzene was 1-pentachlorophenyl-2-chloroethane, I. Bromination, on the other hand, resulted in an almost quantitative yield of the α-substitution product, 1-pentachlorophenyl-1-bromoethane. This difference in the direction of substitution was attributed to a combination of two factors—the greater reactivity of the chlorine atom[2] and steric hindrance about the α-position. Evidence indicating the presence of steric hindrance in systems of this type has been presented in a previous report.[3] We have postulated that with ethylpentachlorobenzene the energy barrier for reaction is smaller for an attack at the α-position but that this position is so shielded sterically by the ortho chlorine substituents that many collisions occur at the β-position before a collision occurs at the α-position. The chlorine atom is so reactive that even a collision at the β-position is sufficiently effective to result in reaction, but with the less reactive bromine atom only a collision at the α-position is effective and no β-bromide is formed.

On the above basis it would be predicted that β-chlorination would be favored over α-chlorination at higher temperatures but that with decreasing temperature the ratio of β- to α-chlorination would decrease. In our previous work we studied the products of the chlorination at both 200 and 68–73°. At both temperatures the predominant product was I. At the higher temperature the only other products isolated were hexachlorobenzene and a highly chlorinated ethylpentachlorobenzene which was not fully characterized. At the lower temperature the other isolable products were hexachlorobenzene and pentachlorostyrene, II, and it was suggested that II arose from decomposition of 1-pentachlorophenyl-1-chloroethane, III, during the distillation process and constituted indirect evidence for the occurrence of some α-chlorination at the lower temperature. In both cases the yield of β-chloride, I, actually isolated was never more than 35% so that the possibility of some α-chlorination even at the higher temperature was not eliminated. It is our present purpose to show that some α-chlorination takes place at both 70–75° and 180° and that the relative amounts of β- and α-chlorination at the two temperatures support the postulated mechanism to account for the difference in the direction of substitution on bromination and chlorination.

If ethylpentachlorobenzene, is chlorinated and then reacts, without purification, with benzene in the presence of aluminum chloride the major product is a mixture of two solids, one melting from 110.5–112.5° and the other from 153–155°. Although the two compounds distil at similar temperatures and pressures they can be readily separated by crystallization and both analyze correctly for $C_{14}H_4Cl_5$. The lower melting one, IV, was synthesized from both 1-pentachlorophenyl-1-bromoethane and pentachlorostyrene by reaction with benzene in the presence of aluminum chloride and must, therefore, be 1-pentachlorophenyl-1-phenylethane. The higher melting product, V, is the isomeric 1-pentachlorophenyl-2-phenylethane and was synthesized by treating I with benzene and aluminum chloride. V can result only from the presence of I in the crude chlorination mixture. IV can result either from III or from pentachlorostyrene. However, since pentachlorostyrene itself probably results from III it is still valid to assume that the amounts of IV and V isolated from the coupling reaction are indicative of the amounts of α- and β-chlorination in the chlorination reaction and we have applied this criterion to the products obtained by chlorination at 180 and 70–75°.

Chlorination of 1000 g. of ethylpentachlorobenzene at 180° followed by coupling with benzene at 50° gave a crude product which yielded five fractions on distillation—a forerun weighing 229 g., the main fraction weighing 546 g., an intermediate fraction of 60 g., a high boiling fraction of 123 g., and a final fraction of 36 g. collected after decomposition of the pot residue had started.

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[1] Ross, Markarian and Nazzewski, THIS JOURNAL, **69**, 1914, 2468 (1947).

[2] Schumacher, *Angew. Chem.*, **53**, 501 (1940).

[3] Ross, THIS JOURNAL, **70**, 4039 (1948).

Crystallization of the forerun yielded two pure products—11 g. of hexachlorobenzene and 110 g. of unreacted ethylpentachlorobenzene. The main fraction on crystallization gave 403 g. of V and 94 g. of IV. From the intermediate fraction the only pure product isolated was 32 g. of V. No more of IV or V was isolated from the subsequent fractions. The over-all yield of monophenyl-substituted ethylpentachlorobenzene is thus 41.4%. Of this 82.1% is the β-substituted product and 17.9% the α-substituted product, and based on this evidence the ratio of β-chlorination to α-chlorination is almost 4.6:1.

The final fraction was largely the product of decomposition and only hexachlorobenzene was isolated from it. The high boiling fraction proved to be a mixture which was particularly resistant to separation. By a combination of crystallization and flotation we succeeded in isolating two pure compounds. One, VI, melted from 143–143.5°, and the other, VII, from 132–133°. Both analyzed correctly for $C_{20}H_{13}Cl_5$, and they must, therefore, be isomeric diphenylethylpentachlorobenzenes. VI was synthesized by treating 1-pentachlorophenyl-1,2-dibromoethane with benzene in the Friedel-Crafts reaction and is 1-pentachlorophenyl-1,2-diphenylethane. VII is either 1-pentachlorophenyl-1,1-diphenylethane or 1-pentachlorophenyl-2,2-diphenylethane. The preponderance of β-chlorination makes the former structure extremely unlikely and we have assigned the latter structure to VII.

The product of chlorination at 70–75° after similar treatment gave three fractions—a forerun of 208 g., the main fraction of 683 g., and a high boiling fraction of 84 g. From the forerun we isolated three compounds; 42.5 g. of unreacted ethylpentachlorobenzene, 11 g. of hexachlorobenzene, and 22 g. of V. From the main fraction we obtained 369 g. of V and 253 g. of IV and from the final fraction we isolated only 5 g. of V and 5 g. of VI. The over-all yield of monophenyl substituted ethylpentachlorobenzene isolated is thus 51%. Of this 61% is the β-substituted product and 33% the α-substituted and the ratio of β-chlorination to α-chlorination is in this case slightly below 1.6:1.

These results clearly indicate that β-chlorination is favored at higher temperatures and that with decreasing temperature the ratio of β- to α-chlorination decreases. This finding is in accord with our postulation that the activation energy for the α-chlorination is lower than for the β-chlorination and lends support to the hypothesis which we previously advanced[1] to account for the difference in the directions of chlorination and bromination of ethylpentachlorobenzene.

Experimental[4]

1-Pentachlorophenyl-2-phenylethane, V.—1-Pentachlorophenyl-2-chloroethane (63 g., 0.2 mole) in 200 cc. of benzene was added dropwise at room temperature over a two-hour period to a stirred suspension of aluminum chloride (2 g.) in 50 cc. of benzene. Stirring was continued until the evolution of hydrogen chloride ceased. The reaction mixture was decomposed with ice and dilute hydrochloric acid. The benzene layer was separated, washed with water, 10% sodium hydroxide, and again with water and finally dried over calcium sulfate. The benzene was removed and the crude product obtained was crystallized from ethanol–benzene (1:1) to yield 52 g. (73.4%) of product melting from 148–153°. Two recrystallizations raised the melting point to 153–155°.

Anal. Calcd. for $C_{14}H_9Cl_5$: C, 47.42; H, 2.62. Found: C, 46.93, 46.99; H, 2.79, 2.86.

1-Pentachlorophenyl-1-phenylethane, IV.—1-Pentachlorophenyl-1-bromoethane (71.5 g., 0.2 mole) in 250 cc. of benzene was reacted with aluminum chloride (2 g.) in 50 cc. of benzene exactly as above. The yield of crude product was in this case quantitative. A sample crystallized two times from ethanol for analysis melted from 110.5–112.5°.

Anal. Calcd. for $C_{14}H_{19}Cl_5$: C, 47.42; H, 2.62. Found: C, 47.01, 47.16; H, 2.95, 2.77.

When pentachlorostyrene was coupled with benzene as above the same product was obtained in 89% yield.

1-Pentachlorophenyl-1,2-diphenylethane, VI.—1-Pentachlorophenyl-1,2-dibromoethane (2 g.) in 40 cc. of benzene was added dropwise to a stirred mixture of aluminum chloride (0.5 g.) in 40 cc. of benzene. The reaction mixture was warmed for three hours after which it was decomposed with water and 10% sodium hydroxide. The benzene layer was separated and dried. The crude product, obtained by removing the benzene, was crystallized from ethanol yielding 1.1 g. of melting point 140–141°. Another crystallization raised the melting point to 143–143.5°.

Anal. Calcd. for $C_{20}H_{13}Cl_5$: C, 55.80; H, 3.04. Found: C, 56.11, 56.30; H, 3.10, 2.94.

Chlorination of Ethylpentachlorobenzene at 70–75°.—Redistilled ethylpentachlorobenzene (1000 g.) was illuminated with a 500-watt bulb and chlorinated at 70–75° to a gain in weight of 136 g. This total product in 750 cc. benzene was added to a stirred suspension of aluminum chloride (62.5 g.) in 1000 cc. of benzene and worked up in the usual manner. Distillation of the total product gave the following fractions: (1) 208 g. of b. p. 100–160° at 0.06 mm.; (2) 683 g. of b. p. 160–187° at 0.06 mm.; (3) 84 g. of b. p. 190–238° at 0.3 mm. Fraction 1 was first separated in the cold into trichloroethylene soluble material and trichloroethylene insoluble material. By repeated crystallization of the insoluble material first from trichloroethylene and then from benzene we isolated pure hexachlorobenzene and V. Removal of the solvent from the trichloroethylene soluble material and repeated crystallization first from benzene-alcohol (2:1) and finally from alcohol alone gave finally additional pure V and ethylpentachlorobenzene. In all we isolated 11 g. of hexachlorobenzene, 42.5 g. of ethylpentachlorobenzene and 22 g. of V from this fraction. Fraction 2 was first redistilled at 0.2 mm. to yield 669 g. boiling from 170–202°. This total product was crystallized by dissolving it in hot trichloroethylene and then adding ethanol until the hot solution began to get cloudy. On cooling V precipitated. The mother liquors were then concentrated until half of the original trichloroethylene had been removed and alcohol was again added to incipient crystallization. Both this crop and a third crop obtained by repetition of this process proved to be 1-pentachlorophenyl-1-phenylethane, IV. In all we obtained 369 g. of V and 253 g. of IV. Fraction 3 was first extracted with 3 300-cc. portions of ethanol and then each extract and the residue were repeatedly crystallized from benzene–ethanol (5:1). In this way we succeeded in isolating 5 g. of pure V and 5 g. of a compound melting from 132–133°. To this latter compound we have assigned the structure VI.

Anal. Calcd. for $C_{20}H_{13}Cl_5$: C, 55.81; H, 3.05. Found: C, 55.42, 55.49; H, 3.10, 2.89.

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[4] The microanalyses were performed by Dr. Carl Tiedcke.

Chlorination of Ethylpentachlorobenzene at 180°.—Redistilled ethylpentachlorobenzene (1000 g.) was illuminated with a 500-watt bulb and chlorinated at 180° to a gain in weight of 132 g. and then reacted with benzene as above. Distillation gave the following fractions: (1) 229 g. of b. p. 100–160° at 0.15 mm.; (2) 546 g. of b. p. 168–180° at 0.2 mm.; (3) 60 g. of b. p. 186–205° at 0.3 mm.; (4) 123 g. of b. p. 210–232° at 0.8 mm.; (5) 36 g. of b. p. 232° at 2.5 mm. Fraction 1 was separated into material soluble in trichloroethylene in the cold and material insoluble in trichloroethylene in the cold. The insoluble material was crystallized from trichloroethylene yielding 11 g. of hexachlorobenzene. The soluble material was crystallized from ethanol yielding 110 g. of ethylpentachlorobenzene. Fraction 2 was crystallized as in the previous case from trichloroethylene-alcohol yielding 403 g. of V and 94 g. of IV. Fraction 3 was also crystallized from trichloroethylene-alcohol and gave only 32 g. of V. When Fraction 4 was crystallized from trichloroethylene–alcohol (1:2) both rods and a powder deposited. The two were separated by floating off the powder with mother liquor and were then crystallized separately to yield pure VII, m. p. 132–133° and pure VI, m. p. 143–143.5°. In all we isolated only 11 g. of VII and 7 g. of VI. Crystallization of Fraction 5 from trichloroethylene–alcohol (2:1) gave only 10 g. of hexachlorobenzene.

Summary

To determine the relative amounts of α- and β-chlorination of ethylpentachlorobenzene at 70–75° and 180° the crude chlorination products were treated in the Friedel–Crafts reaction with benzene and the products of this reaction were then separated by standard methods. To identify the products formed 1-pentachlorophenyl-1-phenylethane, 1-pentachlorophenyl-2-phenylethane and 1-pentachlorophenyl-1,2-diphenylethane were synthesized from starting materials of known structure.

At 70–75° the ratio of β- to α-chlorination is approximately 1.6:1 and at 180° almost 4.6:1, thus indicating a lower activation energy for the α-chlorination. This lends support to the mechanism previously postulated to account for the difference in the direction of chlorination and bromination of ethylpentachlorobenzene.

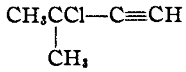
RECEIVED AUGUST 5, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Dialkylethynylcarbinols with Acidic Reagents

BY CHARLES D. HURD AND WARREN D. MCPHEE[1]

Several branched isomers of the formula C_6H_7Cl are reported in the literature. One such is 3-chloro-3-methyl-1-butyne (I) formed by reaction of dimethylethynylcarbinol with hydrochloric acid (at 20°) in the presence of cupric (or cuprous) chloride and ammonium chloride.[2] Apparently it was stable during distillation, b. p. 74–76°. The compound reacted with ammoniacal silver nitrate and underwent hydrolysis in the presence of calcium carbonate to the original carbinol. On standing in the presence of cuprous and ammonium chlorides, (I) gradually rearranged into isomers which were indifferent toward ammoniacal silver nitrate and which were assigned structures II (b. p. 101–104°) and III (b. p. 97.5–98°, d^{20}_4 0.9543). II was indifferent, but III was reactive toward maleic anhydride, giving rise to four products of m. p. 210, 239, 298, 352°. Oxidation of II by potassium permanganate yielded acetone and α-hydroxyisobutyric acid.

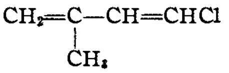


$CH_3CCl—C\equiv CH$ with CH_3 below

I

$(CH_3)_2C{=}C{=}CHCl$

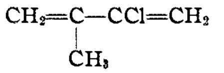
II



$CH_2{=}C—CH{=}CHCl$ with CH_3 below

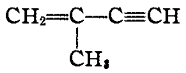
III

Another isomer is 2-chloro-3-methyl-1,3-butadiene (IV). It was prepared by Carothers and Coffman[3] by addition of hydrochloric acid to methylbutenyne (V) in the presence of ammonium chloride and cuprous chloride. It possessed constants (b. p. 93° with some polymerization, 37° (105 mm.), d^{20}_4 0.9593, n^{20}_D 1.4689) which are remarkably close to those given for III. The substance was volatile in steam and polymerizable to a jelly on standing for five days in a tube containing a trace of air. It underwent the Diels–Alder reaction with α-naphthoquinone, the yield of adduct not being given. Oxidation of the adduct gave the known 2-chloro-3-methylanthraquinone, which is confirmatory evidence for structure IV.



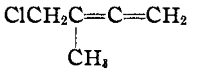
$CH_2{=}C—CCl{=}CH_2$ with CH_3 below

IV



$CH_2{=}C—C\equiv CH$ with CH_3 below

V



$ClCH_2C{=}C{=}CH_2$ with CH_3 below

VI

The present work also deals with a product of formula C_6H_7Cl which was obtained by interaction of hydrochloric acid with dimethylethynylcarbinol. A chloride of structure IV would be expected (via V + HCl) on the basis of the behavior of other related ethynylcarbinols[4] toward acidic reagents. Certain facts agreed with this expecta-

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[1] Holder of Commercial Solvents Corporation Fellowship, 1938–1940. Present address: G. D. Searle and Company, Chicago, Illinois.

[2] Favorskiĭ and Favorskaya, *Compt. rend.*, **200**, 839 (1935); Favorskaya, *J. Gen. Chem.* (*U. S. S. R.*), **9**, 386, 1237 (1939); Favorskaya and Zakharova, *ibid.*, **10**, 446 (1940).

[3] Carothers and Coffman, THIS JOURNAL, **54**, 4071 (1932); Carothers and co-workers, *ibid.*, **53**, 4203 (1931); **54**, 4066 (1932).

[4] Hurd and Jones, *ibid.*, **56**, 1924 (1934); Hurd and Christ, *ibid.*, **59**, 118 (1937).