[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

The Halogenation of Unsymmetrical Diphenylethane[1]

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When 1,1-diphenylethane at 100° in sunlight is treated with chlorine, hydrogen chloride is evolved and a yellow colored, liquid product results. From this material, on distillation, there was isolated unchanged diphenylethane, stilbene, and 1,1-diphenyl-2,2-dichloroethylene. The failure of the product to undergo any appreciable hydrolysis with caustic alkalies, and the absence in it of detectable amounts of 1,1-diphenylethylene and 1,1-diphenyl-2-chloroethylene, indicate that the over-all reaction is a result of stepwise additions of chlorine to intermediate unsaturates produced by the loss of hydrogen chloride.

$$\underset{\text{I}}{(C_6H_5)_2CHCH_3} \xrightarrow{Cl_2} \underset{\text{II}}{(C_6H_5)_2CClCH_3} \xrightarrow{-HCl}$$

$$\underset{\text{III}}{(C_6H_5)_2C{=}CH_2} \xrightarrow{Cl_2} (C_6H_5)_2CClCH_2Cl \xrightarrow{-HCl}$$

$$\underset{\text{IV}}{(C_6H_5)_2C{=}CHCl} \xrightarrow{Cl_2} (C_6H_5)_2CClCHCl_2 \xrightarrow{-HCl}$$

$$\underset{\text{V}}{(C_6H_5)_2C{=}CCl_2}$$

The chloride (II), prepared from the corresponding carbinol, has been described[2] as an uncrystallizable oil which slowly reverts to 1,1-diphenylethylene (III) at ordinary temperatures. The ethylene (III) was observed by Hepp[3] to react vigorously with chlorine at low temperatures giving a product which yielded 1,1-diphenyl-2,2-dichloroethylene (V) on distillation. The initial chlorination, I → II, is, therefore, the slowest reaction and constitutes the rate determining step.

Bromination mixtures, similarly prepared and distilled, gave only small amounts of 1,1,4,4-tetraphenylbutadiene-1,3 and stilbene.

The presence of stilbene in the halogenation mixtures from 1,1-diphenylethane parallels the experience of Kharasch and Clapp[4] who obtained this substance in excellent yields by heating 2,2-diphenylethanol with phosphorus pentoxide, and recognized the change as another case of the Wagner rearrangement. 1,1-Diphenyl-2-chloroethane is known[5] to give stilbene on distillation, and a similar observation has been recorded for 1,1-diphenyl-2-chloroethylene[6] (IV).

1,1-Diphenyl-2,2-dichloroethylene (V) is a remarkably stable substance and requires the action of alcoholic potassium hydroxide at 150° in order to effect its complete hydrolysis. The product, diphenylacetic acid, was similarly prepared by Fritsch and Feldmann,[7] who employed alcoholic sodium ethylate in a sealed tube and describe the removal of unreacted dichloro compound. A diphenoxy derivative was obtained by using sodium phenate in phenol at 225°. The composition of this product, m. p. 111.5°, indicates that hydration of the double bond has occurred to give the diphenylacetal of benzilic aldehyde,[8] since the alternative structure, $(C_6H_5)_2CHC(OH)(OC_6H_5)_2$, might be expected to lose phenol and give the phenyl ester of diphenylacetic acid.[9]

The pyrolysis of 1,1-diphenylethane in a silica tube at 700° gave benzene, toluene, and styrene in small amounts. Goldschmiedt[10] effected this pyrolysis in a pumice-filled tube and reported stilbene as a product, most of the diphenylethane being unchanged.

Experimental Part

1,1-Diphenyl-2,2-dichloroethylene.—Fifty grams of 1,1-diphenylethane[11] in a quartz flask at 100–150° was treated with a slow stream of chlorine during ten hours, the mixture being exposed to sunlight and finally to the light of an electric lamp. The increase in weight was 16 g. The product on distillation evolved abundant fumes of hydrogen chloride and yielded, at 277–308°, 50.8 g. of distillate which soon turned yellow. On adding solid calcium chloride, 1,1-diphenyl-2,2-dichloroethylene crystallized. The mixed solids were collected, freed of adhering oil by suction and pressing, washed with alcohol, and suspended in water. The undissolved material, 13.1 g., was crystallized from alcohol yielding 11.0 g. of 1,1-diphenyl-2,2-dichloroethylene, m. p. 78–79.5°.

The dark yellow oil, 29 cc., remaining from the crystallization with calcium chloride, was rectified at 1 mm. At

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(2) Schoepfle and Ryan, THIS JOURNAL, **52**, 4027 (1930).

(3) Hepp, *Ber.*, **7**, 1411 (1874).

(4) Kharasch and Clapp, *J. Org. Chem.*, **3**, 357 (1938).

(5) Hepp, *Ber.*, **6**, 1439 (1873); Anschütz, *Ann.*, **235** 229 (1886).

(6) Buttenberg, *ibid.*, **279**, 326 (1894).

(7) Fritsch and Feldmann, *ibid.*, **306**, 79 (1899).

(8) Scheibler and Depner, *Ber.*, **68**, 2155 (1935), report a melting point of 103° for this compound.

(9) *Cf. ibid.*, **68**, 2137, 2139, 2144, 2151 (1935).

(10) Goldschmiedt, *ibid.*, **6**, 1503 (1873).

(11) The 1,1-diphenylethane, b. p. 273–274° cor. at 744 mm., used in these experiments was obtained from the Dow Chemical Company. It has an odor remindful of mushrooms.

88° 14.6 cc. of colorless 1,1-diphenylethane, saturated toward bromine water, was recovered. At 113° 3.4 cc. of material passed over and partially crystallized; the crystals, recrystallized from a large volume of boiling alcohol, formed white, glistening plates, m. p. 121–123°, identified as stilbene by comparison with an authentic specimen and by conversion to the dibromide. The residue in the still consisted of crude diphenyldichloroethylene and solidified on cooling.

Bromination of 1,1-Diphenylethane. Stilbene.—To 25 cc. of 1,1-diphenylethane at 100° in a quartz flask suspended in the light from an electric lamp, 18 cc. of bromine was added slowly during three hours. The brown reaction mixture yielded copious fumes of hydrogen bromide on distillation and, at 290–310°, 15 cc. of distillate which crystallized on standing. The crystals were sucked free of oil and recrystallized from alcohol to give 0.4 g. of large plates, m. p. 122–124° alone and when mixed with a known sample of stilbene.

1,1,4,4-Tetraphenylbutadiene-1,3.—1,1-Diphenylethane 25 cc., was brominated as described above but only 10 cc. of bromine was used. Distillation of the product gave a fraction, 277–325°, which slowly crystallized. The crystals, sucked free of oil and recrystallized from acetone–alcohol, gave long, white, flat, glistening needles exhibiting a pale violet fluorescence in diffused daylight, m. p. 204–205° cor. An identical product was obtained from a bromination conducted at 65–70°.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.81; H, 6.19; mol. wt., 358.5. Found: C, 93.45; H, 6.52; mol. wt. (Rast), 364, 361.

The melting point was not changed when the product was mixed with an authentic specimen of 1,1,4,4-tetraphenylbutadiene-1,3.[12]

1,1-Diphenyl-2,2-dichloroethylene crystallizes readily from alcohol in long, white, glistening needles, m. p. 79–80° cor. Melting point depression measurements, using naphthalene and *p*-dibromobenzene as solutes, gave for the cryoscopic constant of the compound respective values of 10.0° and 10.2° (mole/kg.), corresponding to a heat of fusion of 24.7 cal. per g.

Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05; mol. wt., 249. Found: C, 68.04; H, 4.51; mol. wt. (Rast), 271.

Diphenylacetic Acid.—Hydrolysis of 1,1-diphenyl-2,2-dichloroethylene was not effected by twenty-four-hour periods of treatment with alcoholic sodium hydroxide at 100° or aqueous sodium hydroxide at 150°. One gram of diphenyldichloroethylene, 3 g. of potassium hydroxide, and 17 cc. of alcohol were heated in a 38-cc. stainless steel bomb at 150° during twenty-four hours. The reaction mixture was diluted with water, boiled to remove alcohol, and extracted with ether. Acidification of the aqueous portion gave a precipitate of diphenylacetic acid, 0.62 g. (73%), m. p. 144.5–145°; crystallization from 325 cc. of boiling water yielded 0.56 g., m. p. 145–145.5°; recrystallized, m. p. 147–148° cor. The presence of phenol in a methyl alcoholic reaction mixture did not alter the product of hydrolysis.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 78.97, 79.24; H, 5.64, 5.62.

Benzilic Aldehyde Diphenylacetal.—Three-tenths gram of sodium dissolved in 6 g. of warm phenol, and 0.7 g. of diphenyldichloroethylene were heated at 225° during twenty-four hours. The cold reaction mixture, treated with dilute sodium hydroxide solution, left a yellow gummy mass which was washed with water, air-dried, and crystallized from alcohol, yielding 0.09 g. of a brown-tinted mass of small, opaque, chlorine-free prisms, m. p. 111.5–112° cor. The compound is insoluble in hot aqueous sodium hydroxide or hot concentrated hydrochloric acid.

Anal. Calcd. for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 82.34, 81.97; H, 5.60, 5.51.

Pyrolysis of 1,1-Diphenylethane.—The hydrocarbon, 340 cc., was slowly fed into an electrically heated, baffled silica tube at 676–702° during one hour and forty-five minutes. Carbon dioxide, 1.25 cubic feet (35.4 liters) was introduced with the charge, and 2.02 cubic feet (57.2 liters) of mixed gas, containing unsaturated material, resulted. The less volatile products amounted to 308 cc., 311 g., of dark colored oil and on distillation gave, at 71–153°, 64 cc. of a mixture consisting principally of benzene, toluene, and styrene. The viscous black residue, b. p. 258–300°, contained much unchanged diphenylethane and, possibly, some 1,1-diphenylethylene. The benzene–toluene–styrene mixture was cooled and treated with bromine until absorption ceased. The product yielded on distillation 52 cc. of distillate and a black residue which crystallized on cooling. Analysis of the distillate in a column still indicated approximately 42% benzene and 58% toluene. The black residue, freed from oil by suction and pressing, was crystallized from alcohol to give glistening plates, m. p. 71.5–72.5° alone or mixed with an authentic specimen of styrene dibromide.

Summary

The photochemical chlorination of 1,1-diphenylethane at 100°, followed by distillation of the product, gives 1,1-diphenyl-2,2-dichloroethylene and small amounts of stilbene.

The analogous bromination of 1,1-diphenylethane yields stilbene and 1,1,4,4-tetraphenylbutadiene-1,3 in small amounts.

The hydrolysis of 1,1-diphenyl-2,2-dichloroethylene to diphenylacetic acid requires the action of hot alcoholic caustic alkali under pressure.

The pyrolysis of 1,1-diphenylethane yields benzene, toluene, and styrene.

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(12) Valeur, *Bull. soc. chim.*, (3) **29**, 685 (1903).