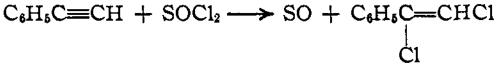
However, in most cases the only compound isolated was the 1,1-diarylvinyl chloride (II), which also represents the main reaction product in the case of 1,1-diphenylethylene. The course of this chlorination is by no means simple. The reaction equation requires the elimination of sulfur monoxide, but so far we have been unable to show its presence among the gaseous reaction products. In some cases higher chlorination products have been found. It is also significant that phenylacetylene (III) is converted into 1,2-dichlorostyrene (IV).



$$C_6H_5C{\equiv}CH + SOCl_2 \longrightarrow SO + C_6H_5\underset{\displaystyle Cl}{\underset{|}{C}}{=}CHCl$$

III IV

In general, the interaction of thionyl chloride with diarylethylenes represents the most convenient method for the preparation of 1,1-diarylvinyl chlorides. In the case of 1,1-di-(*p*-anisyl)-ethylene a nuclear chlorination occurred in addition to the substitution at the β-carbon atom. The product contained three chlorine atoms and its structure is now under investigation.

Experimental[4]

Reaction of Thionyl Chloride with 1,1-Diphenylethylene.—A mixture of the chloride (10 cc.) and diphenylethylene (4 g.) in dry ether (10 cc.), when prepared at 0°, showed no sign of reaction until the temperature of the bath was raised to 55°. The reaction vessel was kept at this temperature, until the evolution of gases ceased (about four hours). The mixture was left overnight, then all volatile components were removed *in vacuo* at room temperature and the residue was poured into a mixture of ice and dilute sodium carbonate. The neutral oil that separated, was extracted with ether and the aqueous layer then acidified with ice-cold hydrochloric acid. The white precipitate had a m. p. of 94–95°; yield 0.85 g. (17%). Two crystallizations from dilute ethanol gave white, silky needles of m. p. 97–98°. 1,1-Diphenylethylene-2-sulfinic acid (I) is a strong acid.

Anal. Calcd. for $C_{14}H_{12}O_2S$: C, 68.9; H, 4.9. Found: C, 68.5; H, 5.3.

The ethereal extract gave 2.2 g. (45%) of an oil, boiling at 150° (1.25 mm.). It solidified after prolonged standing and then showed a m. p. of 41°.[5]

Anal. Calcd. for $C_{14}H_{11}Cl$: C, 78.5; H, 5.1. Found: C, 78.3; H, 5.4.

1,1-Diphenylethylene-2-sulfinic acid (I) was synthesized for comparison in the following way: 1,1-diphenylvinylmagnesium bromide was prepared according to Lipp[6] and dry sulfur dioxide bubbled through the solution for ninety minutes. A white precipitate was first formed, but disappeared again and the solution turned dark red-brown. It was washed with ice-water, dilute hydrochloric acid and again water. Then the acid was extracted with 5% sodium carbonate. Acidification gave 1.8 g. (33%) of acid I, m. p. 96°. One recrystallization from dilute ethanol raised the m. p. to 97°, not depressed by admixture of the acid described above.

Reaction of Thionyl Chloride with 1,1-Di-(*p*-bromophenyl)-ethylene.[7]—A mixture of the ethylene (3.4 g.) and thionyl chloride (10 cc.) was kept at room temperature for twenty-four hours and then refluxed on a water-bath for one hour. No acidic product could be isolated from this reaction. The ethereal solution gave 1.5 g. (40%) of 1,1-di-(*p*-bromophenyl)-vinyl chloride; colorless plates from ethanol, m. p. 107–108°.[8]

Anal. Calcd. for $C_{14}H_9ClBr_2$: C, 45.2; H, 2 Found: C, 45.4; H, 2.6.

Reaction of Thionyl Chloride with Di-(*p*-anisyl)-ethylene.—When the ethylene (10 g.) was dissolved in thionyl chloride (30 cc.), a vigorous reaction took place, but the mixture remained cold. It was left at room temperature for six hours and then refluxed for four hours. The excess thionyl chloride was removed *in vacuo*, the residue dissolved in benzene and washed with an ice-cold soda solution. The alkaline extract gave no precipitate upon acidification. The neutral fraction was distilled *in vacuo:* (1) b. p. 130–150° (4 mm.); starting material, about 1 g.; (2) b. p. 170–180° (0.2 mm.). Upon trituration with methanol 4 g. of crystalline material was obtained. From *n*-propanol the product crystallized in long rods of m. p. 155°. Analysis showed it to contain three chlorine atoms.

Anal. Calcd. for $C_{16}H_{13}O_2Cl_3$: C, 56.0; H, 3.8. Found: C, 56.2; H, 3.9.

Reaction of Thionyl Chloride with Phenylacetylene.—Phenylacetylene (5 g.) and thionyl chloride (15 cc.) were mixed at 0° and the mixture left at room temperature for two hours, then refluxed for four hours. Again no acidic product could be isolated. The neutral portion was purified by distillation, b. p. 216° (700 mm.).[9] The yield of 1,2-dichlorostyrene (III) was 1.5 g. (18%). About 2 g. of phenylacetylene was recovered.

Anal. Calcd. for $C_8H_6Cl_2$: C, 55.5; H, 3.5. Found: C, 55.5; H, 3.5.

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[4] All m. p.s are uncorrected.

[5] Buttenberg, *Ann.*, **279**, 325 (1894), gives a b. p. of 189° (39 mm.) and a m. p. of 42° for 1,1-diphenylvinyl chloride.

[6] Lipp, *Ber.*, **56**, 567 (1923).

[7] This reaction is given as an example for the preparation of a diarylvinyl chloride.

[8] Brand and Amelung, *Ber.*, **72**, 1029 (1939), report m. p. 107–108°.

[9] Dyckerhoff, *ibid.*, **10**, 119 (1877), reports a b. p. of 225–231° (760 mm.).

The Reaction of 1,1-Diarylvinyl Chlorides with Maleic Anhydride

BY FELIX BERGMANN AND JACOB SZMUSZKOWICZ

In an earlier paper[1] we have shown that 1,1-diarylvinyl bromides undergo condensation with maleic anhydride and that the crude intermediate adduct is transformed by heating directly into a fully aromatic derivative of naphthalene-1,2-dicarboxylic acid anhydride (II). In view of the easy preparation of certain 1,1-diarylvinyl chlorides (I) by means of thionyl chloride, described in the foregoing paper,[2] we have investigated the usefulness of such chlorides for the Wagner–Jauregg reaction and observed that the following procedure represents the most convenient route to the anhydrides (II).

The temperature, at which hydrogen chloride is split off is usually 20–30° higher than for the corresponding bromides, but the product is purer and the yield better.

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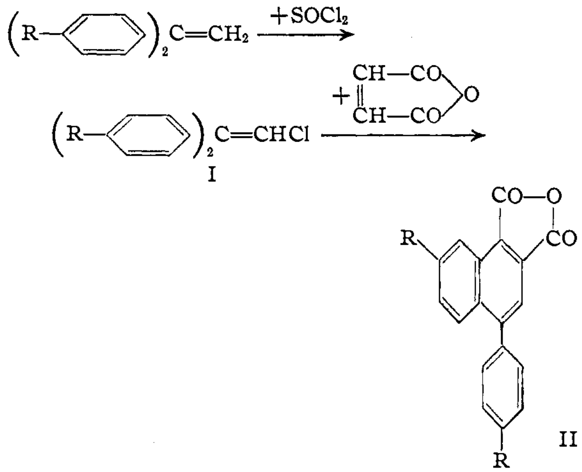
[1] F. Bergmann and Szmuszkowicz, THIS JOURNAL, **69**, 1777 (1947).

[2] Patai and F. Bergmann, *ibid.*, **72**, 1034 (1950).



It will be of interest to investigate, whether diarylvinyl fluorides follow the same course of reaction as the bromides and chlorides.

Experimental

As an example the reaction with 1,1-di-(*p*-chlorophenyl)-ethylene is described:

(1) **1,1-Di-(*p*-chlorophenyl)-ethylene and Thionyl Chloride.**—The ethylene (12.5 g.) and thionyl chloride (30 g.) were refluxed for eight hours. Excess thionyl chloride was removed *in vacuo*, the residue dissolved in benzene, washed, dried and fractionated. A clear greenish oil distilled at 158–162° (1.0 mm.), which crystallized upon trituration with methanol. From the same solvent the di-(*p*-chlorophenyl)-vinyl chloride (I, R = Cl) was obtained in long lancets, m. p. 65–66°; yield, 9.5 g. (68%).

Anal. Calcd. for $C_{14}H_9Cl_3$: C, 59.4; H, 3.2. Found: C, 59.1; H, 3.4.

(2) **Condensation with Maleic Anhydride.**—The above vinyl chloride (1.1 g.) and maleic anhydride (4 g., 10 equiv.) were heated first to 180° for three hours, then to 220° for one hour. The reaction mixture was dissolved in acetic acid and left overnight; 600 mg. (46%) of the anhydride (II, R = Cl) was obtained, which after crystallization from benzene–ligroin formed yellow rods of m. p. 196–197°, not depressed by admixture of the same compound described previously.[3]

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[3] F. Bergmann and Szmuszkowicz, *ibid.*, **70**, 2748 (1948).

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The Copolymerization of Some Fluorinated Olefins

BY MAURICE PROBER

The potential availability of some perhalofluorinated olefins prompted a study of their copolymerization behavior. Each of the fluoroölefins: chlorotrifluoroethylene, unsymmetrical dichlorodifluoroethylene, symmetrical dichlorodifluoroethylene, 1,1,2-trichloro-3,3,3-trifluoropropene, 2,3-dichloro-1,1,1,4,4,4-hexafluorobutene-2,1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene and hexafluorocyclobutene was copolymerized with vinyl acetate, styrene, vinyl chloride, methyl methacrylate and acrylonitrile. There are scattered patent references[1,2,3,4] to some of these copolymers and a recent paper by McBee, Bachman and Hill[5] describes the copolymers of unsymmetrical dichlorodifluoroethylene with vinyl acetate, styrene, butadiene and isoprene.

In this study approximately equal molar quantities of the two monomers were polymerized with benzoyl peroxide, and the composition of the polymer established by elementary analysis. A qualitative picture of the relative reactivities of these olefins is given by the ratios of Table I.

In virtually all of the experiments, the fluorine-free comonomer was better than 90% polymerized, and the relative conversions of fluorinated monomer to polymer follow the order in Table I. The degree of polymerization varies with the comonomer and is greatest with vinyl acetate, styrene and vinyl chloride, and is less extensive with methyl methacrylate and acrylonitrile. The results are also illustrative of the lower reactivity of the 1,2-dichloroethylene as compared to the 1,1-dichloroethylene.

Auxiliary experiments with the fluorinated olefins alone demonstrated that only chlorotrifluoroethylene polymerizes with benzoyl peroxide, indicating that the other polymers are true copolymers. Solubility tests on the chlorotrifluoroethylene polymers indicated that this fluorinated olefin also forms a copolymer.

Experimental

The unsymmetrical dichlorodifluoroethylene, symmetrical dichlorodifluoroethylene, 1,1,2-trichloro-3,3,3-trifluoropropene, 2,3-dichloro-1,1,1,4,4,4-hexafluorobutene-2, and 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene were made available for this study through the courtesy of Dr. B. H. Wojcik and Mr. L. S. Bovier of the Hooker Electrochemical Company. The chlorotrifluoroethylene was purchased from E. I. du Pont de Nemours and Company, and the hexafluorocyclobutene was synthesized according to the procedure of Henne and Ruh.[6]

The fluorinated olefins were washed with concentrated sulfuric acid, water, dried and fractionally distilled. Middle cuts of narrow boiling range were taken for the polymerization runs. The other monomers were purified by rectification of the commercially available pure compounds. The non-volatile monomers and two weight per cent. (based on the total monomer charged) of recrystallized benzoyl peroxide were placed in heavy-walled Pyrex tubes and the volatile monomers distilled in under vacuum. The sample was thawed, refrozen, and sealed under vacuum. Approximately equal molar quantities were selected. The tubes were heated at 60–65° for seventy-two hours. The polymer was then pulverized, and the excess monomer removed by heating in a vacuum. (Some samples were purified by precipitation from solvents, but the analytical results were substantially the same as for vacuum treated samples.) The polymer composition was determined by chlorine analysis (Parr bomb) or by carbon analysis when the former method was not feasible. The experimental error in Table I is approximately ±0.03.

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[1] I. G. Farben, French Patent 796,026 (March 27, 1936).

[2] F. G. Pearson (to American Viscose Corp.), British Patent 584,742 (Jan. 22, 1947).

[3] Imperial Chemical Industries, British Patent 590,390 (July 16, 1947).

[4] E. I. du Pont de Nemours & Co., British Patent 596,943 (Jan. 14, 1948).

[5] McBee, Bachman and Hill, *Ind. Eng. Chem.*, **41**, 70 (1949).

[6] Henne and Ruh, THIS JOURNAL, **69**, 279 (1947).