

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Aromatic Organic Compounds. II. The Fluorination of Hexachlorobenzene

BY LUCIUS A. BIGELOW AND J. HERBERT PEARSON

The purpose of this paper is to record what the writers believe is the first instance to be described of the formation of definite solid products from the reaction of elementary fluorine upon an aromatic organic compound.

The more important literature references in the field have been listed in an earlier communication,¹ but since that time Bockemüller² has published the results of a considerable investigation of direct fluorination in the aliphatic series. The more important phases of this work include the fluorination of normal and isobutyric acids in carbon tetrachloride solution at 0–15°, and of tetrachloroethylene in difluorodichloromethane solution at –80°, leading to the apparent formation of β - and γ -substitution products in the first case, and to monofluoropentachloroethane, difluorotetrachloroethane and difluorooctachlorobutane in the second. The formation of the halogenated paraffins seems very well substantiated, but the other findings, which are directly contrary to all analogy, appear to be insufficiently supported as yet to justify their acceptance without question. No definite results in the aromatic series were reported. Also, Fredenhagen and Cadenbach³ have described very recently a novel apparatus for introducing fluorine into organic compounds, although no definite products were isolated.

In extending our own work, we chose hexachlorobenzene as a starting point, because it has a simple aromatic structure, and because it should be quite resistant to the action of fluorine, partly due to the fact that it contains no hydrogen, and partly on account of its high chlorine content.

When a suspension of this compound in carbon tetrachloride was fluorinated at 0°, the solid gradually disappeared, and when the solvent was removed there remained an oil containing both fluorine and chlorine. This was purified by distillation under reduced pressure, and then subjected to further fluorination, without any solvent, in the special copper reaction vessel which has been

described previously.¹ The resulting colorless oil was then fractionated under reduced pressure, using a Hickman Autovac Still. From two of the fractions, so obtained, one boiling at 135–160° at 1 mm., and the other at 100–115° at 7 mm., there were isolated two solid products, melting, after purification, at 113–114°, and 94–96°, respectively. These gave analytical figures corresponding closely to the formulas $C_6Cl_6F_4$, or tetrafluorohexachlorocyclohexene, in the first case, and $C_6Cl_6F_6$, or hexafluorohexachlorocyclohexane, in the second.

Only small quantities of these compounds were isolated, as compared with the amount of fluorinated material involved; nevertheless their formation, as well as the composition of the oil produced at the same time, furnished the first definite evidence to support the idea that the primary attack of elementary fluorine upon the aromatic organic molecule is one of addition.

The work will be continued.

Experimental

A suspension of 50 g. of tetrachlorobenzene in 500 cc. of carbon tetrachloride was fluorinated for fifteen hours in the glass apparatus described previously,¹ using a current of 7 amps. through the generator. For the first few hours the mixture was kept at 0°, and then allowed to rise to room temperature. The resulting clear solution was washed with 10% sodium carbonate solution, dried and the solvent removed. Nine runs yielded 264 g. of crude oil, which was distilled under reduced pressure to remove hexachlorobenzene. Then 105 cc. of this distillate was further fluorinated for six hours at 0° in the same way, but without solvent, in the special copper apparatus already mentioned. The product, after washing and drying, weighed 174 g. It was distilled in a Hickman Autovac Still, and the portion boiling at 75–140° at 4 mm. collected, which weighed 145 g. and did not crystallize on standing for several days in a refrigerator. To this was added 58 g. more of crude oil, making 203 g. in all, and the mixture was still further fluorinated in the copper apparatus for thirteen hours at 0–20°, and worked up as before. Then 156 g. of the resulting oil was distilled at 7 mm., and divided into several fractions.

Tetrafluorohexachlorocyclohexene.—The portion boiling above 150° at 7 mm., weighing 62.0 g., was redistilled, and a product boiling at 135–160° at 1 mm., weighing 41 g., was finally collected. A sample of this colorless oil weighing 4.4 g. was next emulsified vigorously with 1 cc. of water, and the mixture allowed to stand several days in

(1) Bigelow, Pearson, Cook and Miller, *THIS JOURNAL*, **55**, 4614 (1933).

(2) Bockemüller, *Ann.*, **506**, 20 (1933).

(3) Fredenhagen and Cadenbach, *Ber.*, **67**, 928 (1934).

the refrigerator, when 1.8 g. of solid separated. This was dissolved in 8 cc. of warm 85% alcohol, and on cooling a white solid was deposited which weighed 1.1 g. and melted sharply at 113–114°.

Anal. Calcd. for $C_6Cl_6F_4$: F, 21.1; Cl, 59.0; mol. wt., 361. Found: F, 20.9, 21.0; Cl, 59.0, 59.1; mol. wt. in benzene, 378, 381.

Hexafluorohexachlorocyclohexane.—The portion boiling at 100–115° at 7 mm. (see above) weighed 30 g. When a 5-g. sample of this oil was emulsified vigorously with 1 cc. of water and the mixture allowed to stand in the cold, a small amount of solid separated. A solution of this in warm 85% alcohol deposited a white solid melting at 94–96°.

Anal. Calcd. for $C_6Cl_6F_6$: F, 28.6; Cl, 53.4; mol. wt., 399. Found: F, 28.7, 28.8; Cl, 53.3, 53.6; mol. wt. in benzene, 387, 353.

The analytical method used has been referred to previously¹ but it has been improved somewhat by means of slight modifications. As a further check the fluorine content of pure *p*-fluorobenzoic acid, m. p. 181–182°, has been determined with the following results.

Anal. Calcd. for $C_7H_5O_2F$: F, 13.6. Found: F, 13.8, 13.7, 13.5.

Summary

Hexachlorobenzene has been fluorinated in carbon tetrachloride solution at 0°. Small quantities of tetrafluorohexachlorocyclohexene, $C_6Cl_6F_4$ (m. p. 113–114°), and hexafluorohexachlorocyclohexane, $C_6Cl_6F_6$ (m. p. 94–96°), have been isolated.

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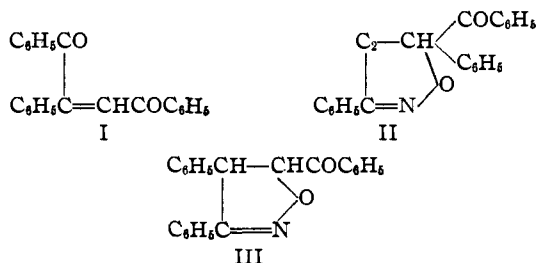
The Reaction between Phenylidibenzoyl ethylene and Hydroxylamine Hydrochloride—A Cyclic Hydroxy Nitrone

BY A. H. BLATT

In 1914 Oliveri-Mandalà and Calderaro¹ reported the results of a study of the reaction between *cis*-phenylidibenzoyl ethylene (I) and hydroxylamine hydrochloride. They obtained from this reaction a yellow crystalline product which had the composition of a monoxime of the diketone and which they considered, because of its almost complete lack of reactivity, to be an isoxazoline—either II or III. Quite incidentally we came across this same yellow product and made some preliminary experiments with it before we were aware of Oliveri-Mandalà and Calderaro's conclusions. Our experiments indicated that the material was unusually reactive. This marked reactivity of the yellow product, its intense color and the fact that it is formed in an acid solution are all difficult to reconcile with its formulation as an isoxazoline. These inconsistencies, coupled with the fact that no information could be found on the behavior of unsaturated 1,4-diketones toward hydroxylamine hydrochloride, have led us to a further study of the reaction between phenylidibenzoyl ethylene (I) and this typical ketone reagent. Certain of the results of that study are reported in the following paragraphs.

It should be stated at the outset that the chemi-

(1) Oliveri-Mandalà and Calderaro, *Gazz. chim. ital.*, **44**, [11] 85 (1914). The first study of this reaction was that of Japp and Klingemann, *J. Chem. Soc.*, **57**, 710 (1890), who employed quite drastic conditions and obtained what were evidently secondary products



cal behavior of the yellow product formed from phenylidibenzoyl ethylene and hydroxylamine hydrochloride is far more complex than was indicated by the earlier work done with it. This product exists in two isomeric forms: one modification, that described by Oliveri-Mandalà and Calderaro, is bright yellow in color, is stable in neutral and acid solution and is easily obtained in a pure condition; the other modification, a very pale yellow solid, is stable only in alkaline or pyridine solution, but it can be obtained in an impure state by careful acidification of its alkaline solutions. We shall consider the alkali stable modification first. This substance is the monoxime of phenylidibenzoyl ethylene (IV). On this point the evidence is quite explicit. Sodium hydroxide or pyridine solutions of the oxime (IV) on treatment with benzoyl chloride furnish a benzoate (V, R = C_6H_5) which can be hydrolyzed to regenerate the oxime (IV). Pyridine solutions of the oxime furnish with acetyl chloride an acetate