CHEMISTRY LETTERS, pp. 99-100, 1972. Published by the Chemical Society of Japan

OCTAFLUOROACRIDONE

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Octafluoroacridone[6] has been conveniently prepared via the reaction between tetrafluorobenzyne and tetrafluoroanthranilic acid, followed by cyclization of the resulting N-tetrafluorophenyltetrafluoroanthranilic acid. Some derivatives of 6 were also prepared.

A method for the preparation of octafluoroacridone was reported by Jenkins and his co-workers very recently1). They obtained low yields of this compound by the tedious electrochemical oxidation of 2-aminooctafluorobenzophenone. On the other hand, it is known2-5) that small amounts of acridones —— unsubstituted, octachloro-, and octabromo-substituted —— are formed during generation of benzynes from their corresponding anthranilic acids by diazotization. The acridones in these cases resulted from the reaction of benzynes with undiazotized anthranilic acids.

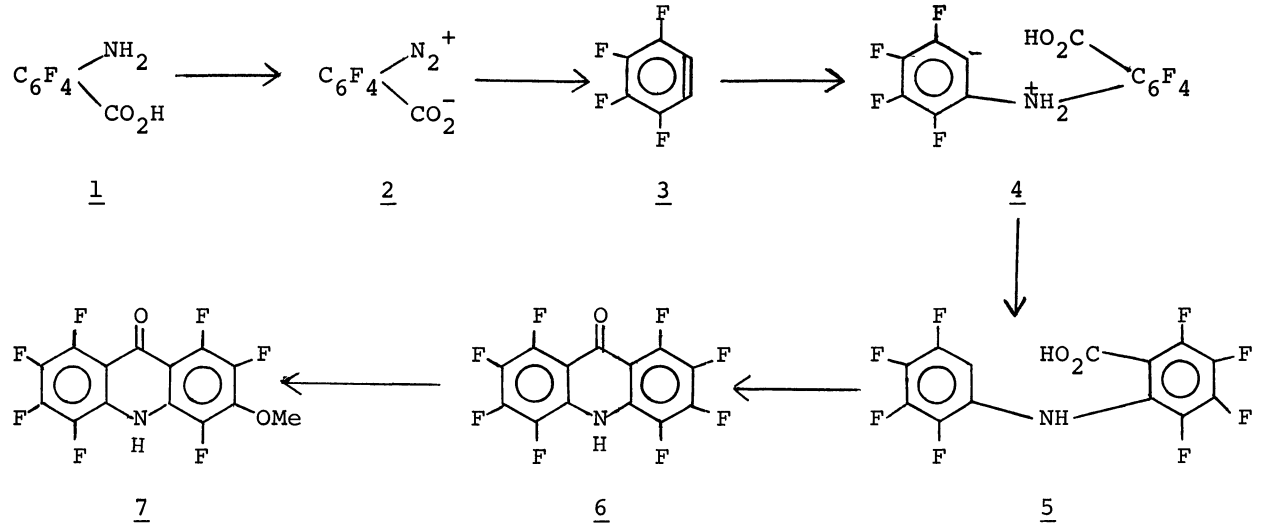
We have previously reported6,7) on the generation of tetrafluorobenzyne from tetrafluoroanthranilic acid, but were unable to detect any compound which resulted from the interaction of tetrafluorobenzyne with tetrafluoroanthranilic acid. We now describe a convenient method for the preparation of octafluoroacridone through this reaction.

When one-half equimolecular amount of n-butyl nitrite was added to a solution of tetrafluoroanthranilic acid [1] in chloroform and the mixture refluxed for a few hours, we obtained the compound[5], mp 187-188°C, as the major product (66%), together with small amounts of octafluoroacridone (2.5%) and 2,3,4,5-tetrafluorophenyl n-butyl ether (4.1%). The formation of the last compound had already been described in our previous paper7).

The structure for the new compound[5] was deduced by ir, nmr, and mass spectral studies and was confirmed to be N-2',3',4',5'-tetrafluorophenyltetrafluoroanthranilic acid. The formation of this compound could be rationalized by the reaction of tetrafluorobenzyne with tetrafluoroanthranilic acid via the intermediate[4].

N-Tetrafluorophenyltetrafluoroanthranilic acid was cyclized to octafluoroacridone[6] when heated with phosphorus oxychloride or with concentrated sulfuric acid, both in quantitative yields. Thus octafluoroacridone has been prepared in two steps starting with tetrafluoroanthranilic acid in >60% overall yield.

Octafluoroacridone readily formed a sodium salt, which gave the N-methyl derivative, mp 167-168°C, when heated with methyl iodide. As for nucleophilic substitution, octafluoroacridone reacted quantitatively with methanolic sodium hydroxide



to give 3-methoxyheptafluoroacridone[7], mp 233-234°C, while dimethylamine or t-butanolic sodium hydroxide failed to react. The structure of 7 was determined by ^{1}H and ^{19}F nmr spectral studies.

Similarly we carried out the reaction of n-butyl nitrite with tetrachloroanthranilic acid in dioxane. Chloroform was not used because of the poor solubility. However, in this case, octachloroacridone (34.6%) and 2,3,4,5-tetrachlorophenyl n-butyl ether (27.8%) were obtained as the major products. It is obvious that the yields of products were somewhat different from those obtained from tetrafluoroanthranilic acid.

Experimental A solution of n-butyl nitrite (0.060 mole) in chloroform (20 ml) was added dropwise into tetrafluoroanthranilic acid (0.10 mole) in chloroform (150 ml) at 60°C during 2.5 hr. After the mixture was refluxed for 2.5 hr, the yellow crystals of 6 (0.43 g) were filtered off. The filtrate was concentrated to a suspension, the resulting crude crystals of 5 (11.8 g, mp 180-183°C) collected and then recrystallized from chloroform to afford the pure product, mp 187-188°C. From the second filtrate tetrafluorophenyl n-butyl ether (0.92 g) was obtained by vacuum distillation.

A mixture of 5 (5.55 g) and conc. sulfuric acid (55 ml) was heated at 120°C for 2 hr, then was thrown into ice water, giving 6 (5.26 g), mp 276-277°C.

Satisfactory analyses were obtained for all compounds mentioned. Details of the structure determinations for 5 and 7 will be described in our later paper.

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(Received November 20, 1971)