[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Positive Bromine from Perfluorinated N-Bromoimides[1]

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The syntheses of perfluorinated N-bromosuccinimide $\overline{COCF_2CF_2CON}Br$ and perfluorinated N-bromoglutarimide $\overline{COCF_2CF_2CF_2CON}Br$ are described. The $-CF_2CO-$ groups attached to the nitrogen make the hydrogen very protonic in the imides and the bromine very positive in the N-bromoimides. Reaction with toluene at room temperature causes ring bromination only, while at 90° side chain and ring bromination occur to comparable extent. No reaction occurs with aqueous silver nitrate. Perfluorinated N-bromoimides can be used as a source of either atomic or positive bromine by control of the experimental conditions.

For free-radical bromination, bromine is used with heat, light or a peroxide, while ionic bromination often requires the presence of a Lewis acid. In N-bromosuccinimide, bromine is generally available as an atom, but in some hydroxylic solvents it can be had in a positive form[3]; this drift away from a negative Br^- ion could be attributed to the elecnegative effect of the imide ring. If this interpretation is correct, perfluorination of the imide ring, which accentuates the induction effect, should enhance the acid character of the N-hydrogen in perfluorinated succinimide and the positive character of the bromine in perfluorinated N-bromosuccinimide. Similar observations should occur with other perfluorinated imides, such as glutarimide. This is here shown to be correct.

The synthesis of N-bromosuccinimide was brought about in three steps: (1) perfluorosuccinic acid was prepared by an improved procedure of the reported method[4,5] by starting from commercial CF_2ClCH_3, perchlorinating to CF_2ClCCl_3 and dechlorinating with zinc to obtain $CF_2{=}CCl_2$ (95% yield for the two steps), cyclodimerizing to $\overline{CF_2CF_2CCl_2C}Cl_2$ (85% yield), dechlorinating to $\overline{CF_2CF_2CCl{=}C}Cl$ (95% yield) and oxidizing to perfluorosuccinic acid (70% yield); (2) the imide function was created by making the diamide from a diester (quantitative), then cyclizing by removing one mole of ammonia with concentrated sulfuric acid (94% yield after reworking intermediates); (3) the N-bromo function was created by making the N-silver derivative, dissolving in trifluoroacetic acid, treating with bromine, filtering off the silver bromide, evaporating the solvent and purifying by sublimation under reduced pressure; this procedure was later modified for conveniency, as described in the experimental part. As shown by nitrogen analysis and by bromine titration with potassium iodide and sodium thiosulfate, the finished material was 99.8% pure. The N-bromo derivative of perfluorinated glutarimide was similarly prepared.

The positive character of the N-hydrogen is shown by quick reaction with an aqueous suspension of silver hydroxide to form the N-silver derivative, and by reaction with diazomethane. The positive character of the N-bromine can be shown in many ways. Aqueous silver nitrate does not cause a precipitate, but alcoholic silver nitrate or aqueous silver nitrite does, showing the oxidizing power of the N-bromine. Iodine is liberated quantitatively from an aqueous solution of iodide and bromine from an aqueous solution of bromide, and they can be titrated with thiosulfate. At room temperature toluene is brominated entirely in the ring, while at higher temperatures progressively larger amounts of benzyl bromide are made, but even at 90° the amount of side chain bromination is not as important as ring bromination. In contrast, plain N-bromosuccinimide or bromine give much higher ratios of side chain bromination at elevated temperatures, while reacting very little or not at all at the lower temperatures where perfluorinated N-bromosuccinimide liberates positive bromine most efficiently; plain N-bromoglutarimide is stated to be ineffective as a brominating agent.[6]

Experimental

Preparation of Perfluorosuccinic Acid.—Modifications from the published[4,5] directions were as follows. Commercial CF_2ClCH_3 (Genetron 101, from General Chemicals Inc., 40 Rector St., New York) is quantitatively chlorinated to CF_2ClCCl_3 over water, with bright illumination; the device previously described[7] is convenient. Transformation of CF_2ClCCl_3 into $CF_2{=}CCl_2$ is done quantitatively with zinc in alcohol in the conventional fashion. Dimerization of the olefin to $\overline{CF_2CF_2CCl_2C}Cl_2$ at 225° for 24 hours in a shaking autoclave is recommended; addition of small amounts of aluminum chloride or benzoyl peroxide is of no practical help. Passage to $\overline{CF_2CF_2CCl{=}C}Cl$ by a conventional zinc in alcohol reaction is quantitative. Oxidation of the double bond by the described basic aqueous permanganate procedure[4,5] gives a 65% yield of perfluorosuccinic acid; by feeding an acetone solution of permanganate to an acetone solution of olefin and keeping the reaction cold, a 74% yield of perfluorosuccinic acid was obtained.

Preparation of the Imide.—Perfluorosuccinic acid was esterified with diazomethane. Nitrosomethylurea (125 g.) in ether was used to prepare a diazomethane solution in the usual way,[8] and perfluorosuccinic acid (55.6 g.) was added in small portions until the yellow color disappeared. Distillation gave 58.5 g. (92%) of dimethyl perfluorosuccinate, b.p. 173–176° (uncorrected), $n^{25}\text{D}$ 1.3555. In another experiment, the diethyl ester[5] was quantitatively prepared by refluxing the acid with ethanol and benzene. A solution of ester (1.5 mole) in ice-cold ether was subjected to a stream of dry ammonia for 2.5 hours. After evaporation on a water-bath, washing with ether and drying, powdery diamide (1.48 mole or 98.6%), m.p. 254–256° (uncorrected) was obtained, which was recrystallized from dioxane and melted at 259.8–260.3°. It is very slightly soluble in cold water, alcohol and ether; it is readily recrystallized from

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[3] S. Winstein, Goodman and Boschan, THIS JOURNAL, **72**, 2311 (1950).

[4] A. L. Henne and R. P. Ruh, *ibid.*, **69**, 279 (1947).

[5] A. L. Henne and W. J. Zimmerschied, *ibid.*, **69**, 281 (1947).

[6] Ziegler, *et al.*, *Ann.*, **551**, 80 (1942).

[7] E. T. McBee, A. L. Henne, H. B. Hass and N. Elmore, THIS JOURNAL, **62**, 3340 (1940).

[8] Blatt, "Organic Syntheses," Coll. Vol. II, p. 165.

hot water or, preferably, dioxane; it readily hydrolyzes in warm dilute alkalies with evolution of ammonia. Its nitrogen content was found to be 14.87%, the correct amount for $C_4F_4O_2N_2H_4$.

To cause cyclization to the imide, the diamide (37.77 g. or 0.2 mole) and 95% sulfuric acid (20.6 g. or 0.2 mole) were combined in a 250-ml. Claisen flask fitted with an ice cooled receiver backed by a Dry Ice-trap. The flask was heated gradually to a temperature of 190° in 1 hour, while the pressure was maintained at 19 to 20 mm. This gave 29.6 g. of crude imide, which was redistilled at 82–87° under 19 to 20 mm. pressure from a 50-ml. Claisen flask with ice receiver and Dry Ice-trap. The redistilled imide (27.8 g. or 0.162 mole) had a neutral equivalent of 172 (theory 171) and a nitrogen content of 8.11% (theory 8.19%). Residues were taken up in absolute alcohol, and all containers were washed with alcohol. After filtration, a little benzene was added and an azeotropic esterification was conducted; when water no longer appeared, the benzene and excess of alcohol were distilled off, and diethyl perfluorosuccinate (11.1 g.) was then recovered by distillation under reduced pressure. This crude product was ammoniated to give 5.3 g. (0.028 mole) of recovered diamide. The imide formation, therefore, took place in 81% conversion and 94.2% net yield. Purification was performed by sublimation at 3.5 mm. pressure on a water-bath kept at 70–80°. The sublimed product had a neutral equivalent of 168, a nitrogen content of 8.19%, a melting point of 66.0–66.5°, and a boiling point of 178° at atmospheric pressure; theory for $C_4F_4O_2NH$ requires 8.19% N and 171 neutral equivalent.

Preparation of Perfluoroglutarimide.—Perfluoroglutaric acid is obtainable in three simple steps from commercial perchlorocyclopentadiene,[9] and for this reason its imide might advantageously replace perfluorosuccinimide. Perfluoroglutaric acid was esterified to its diethyl ester (95% yield) b.p. 203–206°, $n^{22.5}_D$ 1.3598, from which the diamide, m.p. 209.7–210.2°, was obtained quantitatively as above. The cyclization to the imide gave a 70% conversion (89% net yield). Final purification was done by distillation at reduced pressure instead of sublimation to give perfluoroglutarimide b.p. 159°, m.p. 27°, nitrogen content 6.39% (theory 6.33%), neutral equivalent 222 (theory 221).

Methylation of Perfluorosuccinimide.—Perfluorosuccinimide (17.1 g. or 0.10 mole) was dissolved in a minimum amount of ether, and an ether solution of diazomethane was added at ice temperature until the yellow color persisted. Ether was removed by suction with a water aspirator, and a first batch of precipitate filtered off; two more batches of crystals were obtained by further suction. By recrystallization from ether, white crystals (4 g.) m.p. 97.0–97.2° were obtained; evaporation of the mother liquid gave an additional 4 g. of impure product. This methylated derivative has a very high vapor tension, sublimes easily, smells somewhat like chloroform, seems insoluble in water but reacts with it on standing to give a strongly acid solution. Analysis indicates 6.56% N and 33.22% C which does not agree with a monomethyl derivative ($C_5F_4O_2NH_3$ requires 7.57% N and 32.44% C).

Preparation of N-Bromoperfluorosuccinimide.—Silver oxide, Ag_2O (11.6 g. or 0.05 mole), was dissolved in an excess of trifluoroacetic acid, and perfluorinated succinimide (17.1 g. or 0.1 mole) was added; then a solution of bromine (16.0 g. or 0.1 mole) in trifluoroacetic acid was dropped in. The reaction was carried out in a hood, in diffuse light, at room temperature and with constant stirring under a reflux condenser. The theoretical amount of silver bromide precipitated; it was filtered off, washed with trifluoroacetic acid, and the washings were returned to the main solution. The total amount of trifluoroacetic acid used was 418 g., but it is probable that the reaction could be carried out in much less material. The solvent was distilled off at room temperature under 35 mm. pressure into a collecting system made of two receivers cooled in an ice/HCl mixture backed by two Dry Ice-traps, and it was completely recovered. The residue was a white, partly sublimed solid, crude perfluorinated N-bromosuccinimide (21.7 g. or 87% yield) which a titration with KI and thiosulfate showed to contain 29.2% bromine, hence to be 91% pure. This sample was purified by sublimation under 4 mm. pressure to 99.8% purity as measured by a bromine content of 31.90% ($C_4F_4O_2NBr$ requires 31.96% Br); the impurity was found to be mostly unremoved trifluoroacetic acid, and the yield of 87% instead of 100% was attributed to carrying off of vapors by the solvent during its removal. No reliable melting point could be had on account of heat sensitivity.

Preparations in other solvents were much poorer because all the common solvents tried were attacked during the reaction. Other methods of bromination which failed included the use of bromine, bromine and red phosphorus, sodium hypobromite and N-bromosuccinimide.

Bromination of Toluene.—At 24°, 12.5 g. (0.05 mole) of perfluorinated N-bromosuccinimide (abbreviated NBFS) was placed in 50 ml. of toluene; after 16 hours, only 0.0013 mole was left unreacted. The mixture was diluted with ether, then washed with water and a thiosulfate solution to remove most of the imide and to destroy the last traces of its N-bromo derivative. After drying, distillation removed the ether and the excess of toluene, then gave a milky distillate between 155 and 180°, which on cooling separated into two layers, the lower of which solidified. A charred mass of 0.8 g. was left as residue in the flask. The total distillate was agitated with petroleum ether, which left behind 2.4 g. of imide, m.p. 64–67°. After washing with water and drying, the petroleum ether was distilled off, leaving 5.3 g. of material, b.p. 180–185°, n^{20}_D 1.5500, m.p. 5.5°. This is a 62% yield of monobrominated toluene; analysis with silver nitrate indicated that this material contained not more than 0.3% of benzyl bromide. The ratio of ring bromination to side chain bromination is, therefore, about 300/1. At the same temperature, toluene was treated with plain N-bromosuccinimide (abbreviated NBS), but no reaction took place. A similar treatment was then tried with 8.0 g. (0.005 mole) of bromine, which led to the formation of 16% of brominated toluene; this material contained 6.4% of benzyl bromide, indicating that the ring/chain ratio was 15/1.

These three reactions were repeated at 90°: NBFS gave 72% of brominated toluene of which $^1/_3$ was benzyl bromide; NBS gave 80% bromination all of which was in the side chain; bromine gave 76% bromination $^6/_7$ of which was in the chain.

In a third set of experiments, the reagents were mixed and allowed to stand 15 minutes, after which the toluene was brought to reflux. NBFS gave 79% bromination $^1/_{12}$ of which was in the chain; NBS gave 64% bromination all of which was in the chain; bromine gave 73% bromination $^2/_3$ of which was in the chain.

Perfluorinated N-bromoglutarimide was placed in toluene at room temperature; a lively reaction spontaneously raised the temperature to 50°. Monobrominated toluene was obtained in 65% yield, in which the ratio ring to side chain bromination was about 80/1.

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[9] A. L. Henne and W. J. Zimmerschied, THIS JOURNAL, **67**, 1235 (1945), also E. G. DeWitt, Ph.D. dissertation, The Ohio State University, 1949.