EXPERIMENTAL

Reaction of lithium aluminum hydride and p-tert-butylbenzenesulfonyl chloride. Strating and Backer[3] have reported the formation of *p-tert*-butylthiophenol in 76% yield by the treatment of an ethereal solution of *p-tert*-butylbenzenesulfonyl chloride with an ethereal solution of lithium aluminum hydride. A reverse order of addition is used here.

p-tert-Butylbenzenesulfonyl chloride was prepared by the general procedure of Huntress and Carten.[5] A solution of 18.6 g. (0.08 mole) of the sulfonyl chloride in 75 ml. of ether was added slowly with stirring to a suspension of 4.56 g. (0.12 mole) of powdered lithium aluminum hydride in 225 ml. of ether. A nitrogen atmosphere was used. The mixture was stirred for 12 hr. and hydrolyzed with water, followed by dilute hydrochloric acid, and the mixture was then extracted with ether. The ethereal extract was dried and the ether evaporated. The solid residue was extracted with dilute aqueous sodium hydroxide solution and the residue from this recrystallized from absolute ethanol. There was obtained 7.0 g. of solid, m.p. 86–135°. This solid was washed thoroughly with petroleum ether and recrystallized once more from absolute ethanol to yield 3.3 g. (23%) of colorless crystals, m.p. 150–151°.

Anal. Calcd. for $C_{20}H_{26}O_2S_2$: C, 66.30; H, 7.18; S, 17.68. Found: C, 66.14; H, 7.19; S, 17.72.[6]

Preparation of p-tert-butylphenyl p-tert-butylbenzenethiosulfonate. A mixture of 11.6 g. (0.05 mole) of *p-tert*-butylbenzenesulfonyl chloride, 100 ml. of ether, and 4.9 g. of zinc dust was treated dropwise with 32 ml. of concentrated hydrochloric acid, according to the procedure described by Vinkler and Klivenyi[4] for the preparation of the phenyl ester of benzenethiosulfonic acid (thiosulfone) by reduction of benzenesulfonyl chloride. The reaction mixture was stirred at room temperature until all the zinc had dissolved. It was then poured into an excess of cold water and, after the removal of the ether, the precipitated solid was collected by filtration. The solid was washed thoroughly with petroleum ether and recrystallized twice from absolute ethanol, resulting in the isolation of a crystalline solid melting at 150–151°. A mixture melting point with the crystalline solid obtained from the lithium aluminum hydride reduction of *p-tert*-butylbenzenesulfonyl chloride, melting at 150–151°, was 150–151°.

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(5) E. H. Huntress and F. H. Carten, *J. Am. Chem. Soc.*, **62**, 511 (1940).

(6) Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Facile Synthesis of Dihydroisoindole

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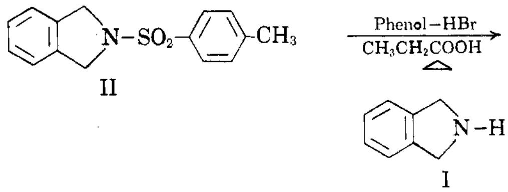
In connection with the synthesis of compounds related to isoindole, it was necessary to prepare gram-quantities of dihydroisoindole (isoindoline) (I). In an effort to avoid the preparation of I by the electrolytic reduction of phthalimide,[1] because of the special apparatus and careful control required, we examined a number of the other methods[2] which have been described. All of them were found to be poor; particularly disappointing was the newest method involving the reduction of phthalimide with lithium aluminum hydride.[3] As a result, a new two-step synthesis of dihydroisoindole was devised, which is based on recent reports[4] that sulfonamides are cleaved rapidly to amines by treatment with hydrobromic acid in the presence of phenol.

When 2-(*p*-tolylsulfonyl)dihydroisoindole (II),[5] which is readily prepared from the easily obtainable substances *o*-xylylene dibromide and *p*-toluenesulfonamide, was heated with a mixture of phenol and hydrobromic acid in propionic acid, dihydroisoindole was obtained in a high state of purity and in yields of 70–78%. This method makes dihydroisoindole easily accessible and appears to be more convenient for small-scale preparations than the electrolytic reduction of phthalimide, which has been, heretofore, the only satisfactory source of dihydroisoindole.



EXPERIMENTAL[6]

2-(p-Tolylsulfonyl)dihydroisoindole (II). This compound was obtained in slightly better yield and in a higher state of purity by modification of the procedure of Fenton and Ingold.[5] The solution, prepared by dissolving 17.0 g. (0.1 mole) of *p*-toluenesulfonamide in a solution of 5.0 g. (0.22 g.-atom) of sodium in 220 ml. of methanol, was added in the course of 40 min. to a stirred and refluxing solution of 26.4 g. (0.1 mole) of *o*-xylylene dibromide in 150 ml. of commercial ethanol. After completion of the addition, the reaction mixture was refluxed and stirred for 2 hr. The suspension was cooled, treated with 100 ml. of water, and neutralized with glacial acetic acid. Refrigeration overnight afforded white needles which, after recrystallization from 95% ethanol, weighed 13.0 g. (48%), and had m.p. 175–176° (dec.) (lit.[5] 176°).

Dihydroisoindole (I). A mixture of 12.0 g. (0.044 mole) of II, 12.0 g. (0.13 mole) of phenol, 90 ml. of 48% hydrobromic acid (freshly distilled from stannous chloride), and 15 ml. of propionic acid was heated under reflux for 2 hr.

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(1) A. Dunet, J. Rollet, and A. Willemart, *Bull. soc. chim. France*, 877 (1950).

(2) S. Gabriel and A. Neumann, *Ber.*, **26**, 521 (1893); R. E. Rose and W. Scott, *J. Am. Chem. Soc.*, **39**, 273 (1917).

(3) A. Uffer and E. Schlittler, *Helv. Chim. Acta*, **31**, 1397 (1948). The authors were able to obtain I in yields of only 3%; A. Dunet, J. Rollet, and A. Willemart (ref. 1) reported a 5% yield from this procedure.

(4) H. R. Snyder and R. E. Heckert, *J. Am. Chem. Soc.*, **74**, 2006 (1952); H. R. Snyder and H. C. Geller, *J. Am. Chem. Soc.*, **74**, 4864 (1952); D. I. Weisblat, B. J. Magerlein, and D. R. Myers, *J. Am. Chem. Soc.*, **75**, 3630 (1953).

(5) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 3295 (1928).

(6) Melting points are corrected and boiling points are uncorrected. Analyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass., and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

in an atmosphere of nitrogen. The wine-colored reaction mixture was cooled to room temperature and, after being washed twice with 200-ml. portions of ether, was added drop-wise to a stirred, ice-cold solution of 75 g. of sodiun hydroxide in 200 ml. of water. The mixture was extracted with five 150-ml. portions of ether and the combined ethereal extract was dried over potassium carbonate, after being washed with water. Removal of the solvent *in vacuo* and distillation of the residue through a semimicro column afforded 3.8 g. (72%) of dihydroisoindole as a colorless oil, b.p. 115° at 30 mm., n_D^{24} 1.5698, d_4^{20} 1.081, which solidified in the refrigerator, m.p. 16.0–16.5°. The *picrate*, obtained as silky, yellow needles from ethanol, had m.p. 195–196° (reported[5] 196–197°).

The *2-trifluoroacetyl derivative* of I was prepared by treating an ethereal solution of dihydroisoindole with a slight excess of methyl trifluoroacetate and allowing the mixture to stand overnight at room temperature. Evaporation of the solvent *in vacuo* followed by recrystallization of the residue from 50% methanol yielded long, felted needles, m.p. 80.5–81.0° (with sublimation).

Anal. Calcd. for $C_{10}H_8F_3NO$; C, 55.82; H, 3.75; F, 26.49; N, 6.51. Found: C, 55.9; H, 3.7; F, 26.0; N, 6.6.

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Thermal Reactions of Perfluorobutyne-2 and Perfluoropropene[1]

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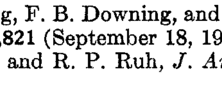
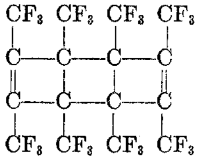
The tendency toward formation of the cyclobutane ring and the thermal stability of this structural conformation has been noted in several instances in studies of reactions of fluorocarbons with C—C multiple bonds. For example, tetrafluoroethylene readily forms perfluorocyclobutane when heated under pressure.[2] Formation of a cyclobutane ring also occurs in the dimerization of trifluorochloroethylene to give 1,2 dichlorohexafluorocyclobutane.[3] Miller,[4] by heating the unsaturated dimer of perfluorobutadiene, produced a saturated dimer believed to have the fused tricyclic structure (I).


I

We have found that perfluorobutyne-2 and perfluoropropene undergo a cyclization reaction that appears to be similar to that of the previously studied fluorocarbon olefins.

Perfluorobutyne-2, $CF_3C\equiv CCF_3$, forms a white, crystalline tetramer when heated under autogenous pressure. The solubility properties of this product are interesting and somewhat unusual for fluorocarbons. It is slightly soluble in ethylene dichloride, carbon tetrachloride, ethyl alcohol, and benzene at room temperature. The solubility in each of these solvents increases markedly with increasing temperature. This compound is very soluble in acetone and in ethyl ether at room temperature. It does not show unsaturation by reaction with potassium permanganate in acetone but its infrared spectrum shows a weak absorption band at 5.72μ, which is in the region expected for C—C unsaturation in fluorocarbons.

A fused polycyclic structure (II) is proposed for this tetramer of perfluorobutyne-2 on the basis of data obtained to date. Its crystallinity and other physical properties seem to favor this symmetrical type of structure. C—C double bonds in the position shown would not be expected to react readily with potassium permanganate under the mild conditions employed. The infrared absorption spectrum[5] shows the following peaks (microns): 5.72, weak; 6.75, weak; 7.15, moderate; 7.30, moderate; 7.47, moderate; 7.73, strong; 8.10–8.40, (unresolved) very strong; 8.52, very strong; 9.53, very strong; and 14.85, moderate.


II

The saturated cyclic dimer of perfluoropropene has not been described previously although Haszeldine[6] has reported formation of a trimer, tetramer, and pentamer from ultraviolet irradiation of perfluoropropene. We have found that perfluoropropene can be thermally dimerized by heating under autogenous pressure. The infrared spectrum of the saturated product, perfluorodimethylcyclobutane, shows the following peaks (microns): 7.22, moderate; 7.40, strong; 7.55, strong; 7.68, very strong; 7.95, very strong; 8.20, very strong; 9.38, weak; 9.58, weak; 11.00, strong; 11.35, strong; 13.45, weak, 13.63, moderate; and 13.82; moderate. This perfluoropropene dimer shows no unsaturation by infrared analysis, permanganate oxidation, or halogen addition. No higher boiling fractions that might indicate the presence of a linear dimer or higher polymers were found in the reaction product. Data is not yet available to show whether this compound as produced is a head-head dimer (III)

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[1] This work was supported by the Office of Naval Research under Contract N-onr 580(03); NR 356-333 with the University of Florida. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] A. F. Benning, F. B. Downing, and R. C. McHarness, U. S. Patent **2,384,821** (September 18, 1945).

[3] A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[4] W. T. Miller, *Preparation, Properties and Technology of Fluorine and Organic Fluoro Compounds;* McGraw-Hill Book Co., N. Y. (1951), p. 604.

[5] Infrared spectrum taken in carbon tetrachloride with a Perkin-Elmer Model 21 double beam spectrophotometer.

[6] R. N. Haszeldine, *J. Am. Chem. Soc.*, **75**, 3559 (1953).