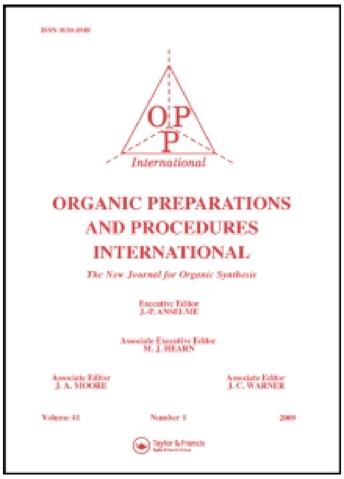

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THE IODINATION OF FLUORENE TO 2,7-DIIODOFLUORENE

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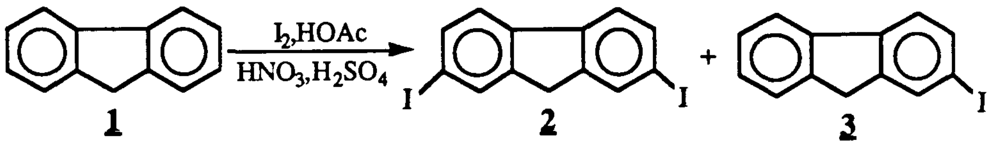
2,7-Diiodofluorene (2) was required as a mass spectrometry standard. The general routes for its synthesis from readily available starting materials are iodination of fluorene in the presence of a variety of oxidizing agents[1,2] and the Sandmeyer reaction of 2,7-diaminofluorene.[2,3] The latter reaction, although useful for the preparation of 1,5-diiodonaphthalene from 1,5-diaminonaphthalene in 50-70% yield, failed to give more than 10-15% of 2 on repeated attempts using commercial 2,7-diaminofluorene; this low yield is consistent with an earlier report.[2] In addition, the cost of this starting material and its toxicity dictated a search for other synthetic routes.

Bis[trifluoroacetoxy]phenyliodide (BTAPI) in carbon tetrachloride and in chloroform was tried since this reagent was reported to be useful for iodinating aromatic compounds.[4] Using BTAPI, 4,4'-diiodobiphenyl was prepared in 85% yield but this reagent failed to give more than 10-15% of 2. The use of I_2/Al_2O_3, in the iodination of aromatic hydrocarbons, has recently been reported.[5] This procedure was not used.



The best results for the preparation of 2 were through iodination of 1, as shown above.[1] In the presence of a 1:10 mixture of red fuming nitric acid and sulfuric acid in acetic acid, 1 is converted to 2 in 79% crude yield. After Soxhlet extraction, a 50% yield was realized. These conditions have been reported to produce I_3^+ which is considered to be the attacking species.[6] Fuming nitric acid is essential because the use of 70% nitric acid (1.42 sp gr) gave mainly 2-iodofluorene (2:3; 13.5/78.5). The ^{1}H-and ^{13}C-NMR spectra of 2 obtained from all sources were identical. Earlier workers included use of carbon tetrachloride as a reaction solvent.[1] However, in carbon tetrachloride, the yield of purified 2 was reduced to 20-25% as compared to 50% using the present procedure. We have no explanation of why the presence of carbon tetrachloride in the reaction mixture is deleterious. Unfortunately, no experimental details regarding the use of carbon tetrachloride, other than the reaction temperature, were given. The isolation and purification consisted of diluting the reaction mixture with water, filtering and recrystallizing from suitable solvent.[1] This procedure was modified by washing with 5% KI in water, 5% sodium thiosulfate in water, air drying and extracting in a Soxhlet apparatus containing neutral alumina layered over silica and using refluxing commercial hexanes as solvent.

EXPERIMENTAL SECTION

2,7-Diiodofluorene. - In a two-necked, 1-L flask, equipped with a thermometer and magnetic stirrer was added fluorene (16.60 g, 0.1 mol), finely divided iodine (25.4 g, 0.1 mol) and 400 mL acetic acid. A mixture of 2 mL of red fuming nitric acid and 20 mL of sulfuric acid (96%, 1.85 sp gr) was added dropwise during 25 min to the stirred reaction mixture. The reaction mixture was stirred at 30-35 °C (water bath) for a total of 30 min; then diluted with 2.5 L of distilled water and the resulting precipitate was collected and washed with 50 mL cold acetic acid to remove unreacted fluorene. The precipitate was then washed with 100 mL of 5% potassium iodide solution and then with 100 mL of 5% sodium thiosulfate, followed with water. The precipitate was air dried to constant weight and then Soxhlet extracted with isohexane using a 2.5 cm bed of neutral alumina layered over 7.5 cm of silica gel. On cooling, the extract, 20.8 g (50%) of light yellow colored needles, mp. 205-212°, were obtained. Two crystallizations from ethanol gave straw-colored needles of 2, mp. 210-212 °, lit.[1] mp.215 °.

^{1}H-NMR(CDCl$_3$):δ 7.82 (s,2H), 7.72 (d,2H) 7.54 (d,2H), 3.82 (s,2H); ^{13}C-NMR(CDCl$_3$): δ 144.8, 140.3, 135.9, 134.1, 121.5, 92.4, 36.2.

The crude reaction product was separated on a 1.8 meter X 2mm I.D. 10% SP-2100 column and leaked through a jet separator into a VG7070 mass spectrometer operated at 3K resolution and using a scan time of 1 second/decade; the data were taken using a Kratos preprocessor interface and DS55 software. In addition to **2** and **3** (77.1% and 11.3% respectively), nitrofluorene (3.8%) and nitroiodofluorene (7.7%) were identified.

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