by phenyl (i.e. 3a to 3c, 3e to 3g, 3j to 3k) led to a decrease in the pK_a of the salt, usually by about one pK_a unit. Thereby were provided additional examples of an effect first noted by us in 1960 (10) and subsequently amplified in our more recent work (7). This increase in acidity has been attributed by us (7) to the powerful inductive withdrawal effect of the phenyl group (relative to alkyl) which decreases the electron density on the heteroatom. The lowered electron density on the heteroatom results in better $p\pi - d\pi$ overlap, in other words, better stabilization of the ylid by the heteroatom group. The replacement of methyl by *n*-butyl also

led to a decrease in the pK_a of the 'onium salts (3). This implies that *n*-butyl is electron-withdrawing (or less electron-donating) with respect to methyl. It is worth noting that the same effect has been noted by Grim et al. (11) in comparing the effect of methyl and *n*-butyl on the shielding of phosphorus in phosphonium salts as detected by ³¹P nuclear magnetic resonance spectra. These authors attributed the effect to hyperconjugation differences between the two alkyl groups. We intend to explore this phenomenon further.

Although there is no exact quantitative data available, it appears that 'onium ylids with similar substitution follow a reactivity sequence of As > P > S, at least as measured by reaction with carbonyl compounds. From the pK_a data in Table I it is apparent that a basicity sequence for the same ylids is As > P > S. Thus, for similarly substituted ylids, but with different

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heteroatoms, nucleophilicity seems to parallel basicity. Fliszar et al. (6) have demonstrated such a quantitative relationship, but only within the triphenylphosphoniumphenacylide series (2, $X = (C_6H_5)_3P$). However, for some as yet unknown reason, this kind of relationship seems not to hold between dimethylsulfoniumfluorenylide and triphenylphosphoniumfluorenylide in light of their new pK_a values (10). We are exploring this aspect further.

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Fluoranthene studies. III. A synthesis of 3-bromo-6-nitrofluorenone

E. H. CHARLESWORTH and P. MATHIAPARANAM

Department of Chemistry, The University of Manitoba, Winnipeg, Manitoba

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A synthesis of 3-bromo-6-nitrofluorenone has been accomplished by the diazotization and Pschorr cyclization of 2-amino-4-bromo-4'-nitrobenzophenone, the synthesis of which is described. The identity of the above bromonitrofluorenone with the degradative oxidation product of 9-bromo-2-nitrofluoranthene establishes unequivocally the structure of the latter substance.

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By degradative oxidation of what was presumably 9-bromo-2-nitrofluoranthene (1), Charlesworth and Dolenko (1) obtained a previously unrecorded bromonitrofluorenone. Other evidence suggested that the bromine was in the 9-position of the fluoranthene nucleus and thus CANADIAN JOURNAL OF CHEMISTRY. VOL. 46, 1968



that the degradation product was 3-bromo-6nitrofluorenone (2). It seemed desirable to synthesize this substance by an unambiguous method which would leave no doubt as to its structure and that of the 9-bromo-2-nitrofluoranthene.

From the variety of methods in the literature for the synthesis of substituted fluorenones, the most hopeful seemed to be the general method of Miller and Bachman (2) which involves a Pschorr cyclization of 2-aminobenzophenones. Two variations of the scheme were attempted. 4-Nitroanthranilic acid was tosylated and converted to its acid chloride. The tosylated acid chloride, however, failed to go into a Friedel-Crafts reaction with bromobenzene. The second variation was successful. 4-Amino-2-methyl-4'nitrobenzophenone(3) was prepared by a Friedel-Crafts reaction following the directions of Mehta, Sacha, and Patel (3). By a Sandmeyer reaction the amino group was replaced by bromine (4). The methyl group was oxidized to carboxyl (5) and then by means of a Curtius degradation the 2-amino compound 8 was finally obtained. Diazotization of 8 and Pschorr cyclization yielded the 3-bromo-6-nitrofluorenone (2), somewhat purer than that obtained by Charlesworth and Dolenko (1). No depression in melting point occurred on mixing and both samples gave identical infrared spectra.

We were unable to obtain the amine 8 by the Hofmann degradation of the amide 7. An acidic compound was produced which might possess the pseudo structure 10, as suggested for similar compounds by Bhatt (4).

Experimental

A supply of 4-amino-2-methyl-4'-nitrobenzophenone

(3) was prepared by a Friedel-Crafts reaction between *p*-nitrobenzoyl chloride and *m*-acetotoluidide according to the directions of Mehta, Sacha, and Patel (3). This product was obtained as red, elongated prisms which melted at 164-166 °C. The original authors reported a melting point of 159-161 °C.

 $R_2 = CONH_2$ $R_2 = NH_2$ $R_2 = OH$

Anal. Calcd. for C14H12O3N2: N, 10.93. Found: N, 10.98.

4-Bromo-2-methyl-4'-nitrobenzophenone (4)

4-Amino-2-methyl-4'-nitrobenzophenone (16 g) was dissolved in hot hydrobromic acid (75 ml, 48%) and cooled to 0 °C by the addition of ice. The amino compound was diazotized by the slow addition of a solution of sodium nitrite (6.0 g) in water (30 ml). After standing at 0 °C for 15 min, the diazonium salt solution was poured into a boiling solution of cuprous bromide (92 g) in hydrobromic acid (200 ml, 48%) at such a rate that the boiling was not interrupted. The boiling was continued for a further 30 min. After cooling and dilution with water, a reddish-white solid precipitated, which was filtered, dried, and extracted with benzene. The benzene solution was washed successively with solutions of sodium sulfite (5%)and sodium hydroxide (10%) and finally with water. After drying with calcium chloride and removal of the benzene, the crude residue was crystallized from acetone. The 4bromo-2-methyl-4'-nitrobenzophenone (17.2 g) melted at 110–111 °C.

Anal. Calcd. for C₁₄H₁₀O₃N Br: N, 4.38; Br, 25.0. Found: N, 4.27; Br, 25.1.

2-(p-Nitrobenzoyl)-5-bromobenzoic acid (5)

4-Bromo-2-methyl-4'-nitrobenzophenone (15.6 g) was dissolved under reflux in hot acetic acid (45 ml). An oxidizing solution of chromium trioxide (13.2 g), acetic acid (45 ml), concentrated sulfuric acid (15 ml), and water (30 ml) was added to the ketone at such a rate that the temperature was kept just below the boiling point. The mixture was refluxed for 3 h, cooled, and diluted with water. The precipitated solid was filtered and washed with water until white. It was suspended in hot water and potassium hydroxide solution added to dissolve as much of the acid as possible. The mixture was filtered and acidified with concentrated hydrochloric acid. The precipitated acid was collected and recrystallized from ethanol. It (13.2 g) melted at 194-196 °C.

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Anal. Calcd. for C14H8O5N Br: N, 4.00; Br, 22.8. Found: N, 3.96; Br, 23.0.

5-Bromo-2-(p-nitrobenzoyl)benzoyl Chloride (6)

The acid chloride was prepared from the acid (5.5 g) by treatment with thionyl chloride (10 ml) in the usual manner in benzene (40 ml) as solvent. 5-Bromo-2-(p-nitrobenzoyl)benzoyl chloride (4.2 g) melted at 124-126 °C.

Anal. Calcd. for C14H7O4NClBr: N, 3.80; Cl, 9.62; Br, 21.7. Found: N, 3.68; Cl, 9.37; Br, 21.9.

5-Bromo-2-(p-nitrobenzoyl)benzamide (7)

The above acid chloride (8.5 g) was dissolved in benzene and with cooling slowly treated with ammonia solution (100 ml, d 0.88). The crude pasty mass of amide was filtered and washed several times with hot water. It was recrystallized from ethanol. 5-Bromo-2-(p-nitrobenzoyl)benzamide (8.0 g) melted at 239-240 °C.

Anal. Calcd. for C14H9O4N2Br: C, 48.2; H, 2.60; N, 8.03; Br, 22.9. Found: C, 47.9; H, 2.55; N, 8.04; Br, 22.9.

2-Amino-4-bromo-4'-nitrobenzophenone (8)

(a) By the Curtius Method

Sodium azide (0.75 g) activated as described (6) was dissolved in water (2.0 ml) and added to a cold solution of 5-bromo-2-(p-nitrobenzoyl)benzoyl chloride (1.5 g) in acetone (20 ml). The reaction mixture was stirred for 15 min and the solid which had precipitated was filtered and dried in vacuo. The acid azide (1.5 g) thus obtained melted at 99-101 °C.

The dry azide was dissolved by refluxing for 2 h with benzene (25 ml). After cooling, potassium hydroxide solution (15 ml, 50%) was added and the mixture was warmed on a water bath during which time a yellow solid separated. The benzene was removed by vacuum distillation and the suspension cooled and filtered. The solid was treated with hot concentrated hydrochloric acid and the hot solution filtered through a sintered glass funnel. After cooling the amine was precipitated by the addition of 10% sodium hydroxide solution, collected, and dried. It was recrystallized from pyridine as bright-yellow needles (1.2 g) which melted at 213-214 °C.

Anal. Calcd. for C13H9O3N2Br: N, 8.73; Br, 24.9. Found: N, 8.71; Br, 24.4.

(b) By the Hofmann Method

A number of attempts to obtain the amine 8 by the Hofmann degradation of the amide 7 with sodium hypobromite or sodium hypochlorite were unsuccessful. Acidification at the end of the treatment gave a substantial yield of a product which crystallized from alcohol as yellow plates, m.p. 232-233 °C. This substance has not been identified. Color, melting point depression on mixing, and its greater solubility in sodium hydroxide solution indicate it is not the original amide. It is acidic (soluble in sodium hydroxide) and not identical with the amine obtained by the Curtius method. It might have the tautomeric pseudo structure 10 as suggested for similar compounds by Bhatt (4).

Anal. Calcd. for $C_{14}H_9O_4N_2Br$ (amide or ψ -amide): C, 48.2; H, 2.60; N, 8.03; Br, 22.9. Found: C, 48.3; H, 2.77; N, 7.99; Br, 23.1.

3-Bromo-6-nitrofluorenone (2)

2-Amino-4-bromo-4'-nitrobenzophenone (0.8 g) was dissolved in concentrated sulfuric acid (2.0 ml) and a few drops of water were added. The amine sulfate separated as a fine suspension which was cooled to 0 °C. An icecold solution of sodium nitrite (0.2 g) in water (2.0 ml) was added. The amine sulfate first dissolved and a solid compound separated. On warming, this product dissolved and then a yellow solid separated which was collected by filtration and washed with sodium hydroxide solution (10%) and then with water. The dried 3-bromo-6-nitrofluorenone crystallized from nitrobenzene as brightyellow plates (0.3 g) which melted at 339-341 °C.

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Anal. Calcd. for C13H6O3NBr: N, 4.61; Br, 26.3. Found: N, 4.72; Br, 26.2.

There was no depression of melting point of this product on the addition of a little of the sample produced by Charlesworth and Dolenko (1). Comparison of the infrared spectra of the two specimens also confirmed their identity.

The oxime of 3-bromo-6-nitrofluorenone was prepared by refluxing the ketone with a solution of hydroxylamine hydrochloride in ethanol for 2 h. On cooling a paleyellow product separated. After recrystallization from ethanol it melted at 269-270 °C.

Anal. Calcd. for C13H7O3N2Br: N, 8.78; Br, 25.0. Found: N, 8.70; Br, 25.4.

Acidification of the sodium hydroxide washings from the preparation of the ketone mentioned above gave a yellow product (0.26 g) which crystallized from aqueous ethanol in light-yellow needles. These melted at 150-151 °C and were presumably 2-hydroxy-4-bromo-4'nitrobenzophenone (9) produced in a side reaction.

Anal. Calcd. for C₁₃H₈O₄N Br: N, 4.35; Br, 24.8. Found: N, 4.55; Br, 24.9.

4-Nitro-2-(p-toluenesulphonamido)benzoic Acid

(4-Nitro-p-tosylanthranilic acid)

This previously unreported derivative was made from 4-nitroanthranilic acid and p-toluene sulfonyl chloride following the directions of Scheifele and DeTar (5). The crude product crystallized from ethanol in pale-yellow plates, m.p. 225-226 °C.

Anal. Calcd. for C14H12O6N2S: N, 8.33; S, 9.52. Found: N, 8.35; S, 9.46.

Friedel-Crafts reactions with phosphorus pentachloride, aluminium chloride, and bromobenzene failed to give any 2-amino-4-bromo-4'-nitrobenzophenone (8).

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