to react for 12 h. After dropwise addition of 200 mL of saturated aqueous NH_4Cl, five 100-mL extractions with ether were carried out, the ethereal extracts were combined, and the ether was distilled off. The resultant imine was subjected to a 5-h reduction by 2.08 g (0.300 g-atom) of lithium in 500 mL of methylamine. The solution was hydrolyzed (200 mL of water) and extracted (five 100-mL portions of ether), and the combined extracts were dried (Na_2SO_4). After the ether was stripped off, the product was distilled at atmospheric pressure to give 19.1 g (76.4%) of *N*-methyldecylamine [bp 216–218 °C (lit.[3] bp 224 °C)]. *N*-Methyldecanamide (3.90 g, 14.4%) was obtained from the distillation residue.

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Registry No. *N*-Methylpentanamide, 6225-10-1; *N*-methyloctanamide, 1119-57-9; *N*,*N*-dimethylpentanamide, 6225-06-5; *N*,*N*-dimethylhexanamide, 5830-30-8; *N*,*N*-dimethyloctanamide, 1118-92-9; *N*,*N*-dimethyldecanamide, 14433-76-2; *N*,*N*-diethyldecanamide, 2602-61-1; *N*,*N*-dicyclohexylpentanamide, 59048-92-9; pentanal, 110-62-3; *N*-octylidenemethylamine, 53106-86-8; hexanal, 66-25-1; decanal, 112-31-2; *N*-methyldecanamide, 23220-25-9; 1-octanol, 29063-28-3; *N*-methyloctylamine, 2439-54-5; *N*-methyldecylamine, 7516-82-7; dicyclohexylamine hydrochloride, 4693-92-9; octanal, 124-13-0.

Reactions of Some Aromatic Nitro Compounds with Alkali Metal Amides

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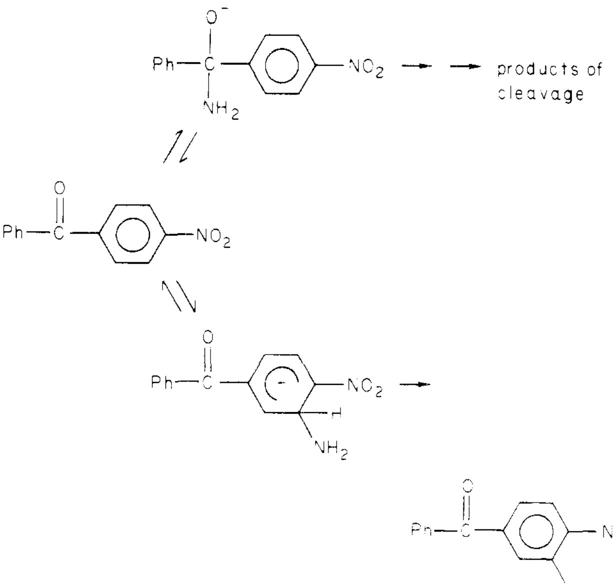
During recent studies on cleavage of substituted benzophenones by potassamide in ammonia,[1] we noted an interesting competing reaction in the case of 4-nitrobenzophenone. This has prompted further examination of this and similar reactions of a number of other aromatic nitro compounds.

4-Nitrobenzophenone would be expected to undergo reversible addition of amide ion at the carbonyl group and eventually to yield benzoic acid and nitrobenzene if cleavage followed.[2] Benzoic acid was in fact isolated from a somewhat sluggish reaction of 4-nitrobenzophenone and potassamide in ammonia from which 45% of the ketone was recovered, but no nitrobenzene was detected. This became understandable when it was noted that nitrobenzene was readily consumed under the reaction conditions to give a complex mixture of products. Competing with the cleavage was an unexpected reaction leading to a product $C_{13}H_{10}N_2O_3$ which contained amino, carbonyl, and nitro groups (^1H NMR and IR spectra). Examination of the mass spectrum permitted elaboration of the formula to $C_6H_5COC_6H_3(NH_2)(NO_2)$ from the breakdown pattern $M^+ \rightarrow C_6H_5CO$ (*m/e* 105). The choice between 2-amino- and 3-amino-4-nitrobenzophenone was determined in favor of the 3-substituted compound from the breakdown pattern $M^+ \rightarrow C_6H_5COC_6H_3(NH)(NO)$ (*m/e* 225), the result of loss of OH between the amino and nitro groups via a cyclic transition state (ortho effect).[3] The matter was clinched by comparison with an authentic sample of the 2-amino compound[4] which showed a different mass spectral breakdown (specifically, no peak at *m/e* 225), a different IR spectrum, different chromatographic (TLC) characteristics, and a melting point depression on admixture with the compound obtained from 4-nitrobenzophenone. Similar considerations (^1H NMR and mass spectra) allow the likely identification of a byproduct in the reaction as 3-hydroxy-4-nitrobenzophenone, although this compound was not isolated in a pure condition [breakdown patterns: $M^+ \rightarrow C_6H_5CO$ (*m/e* 105), $M^+ \rightarrow C_6H_5COC_6H_3(O)(NO)$ (*m/e* 226), no peak observed at *m/e* 165 as would be expected[5] for the 2-hydroxy isomer].

Scheme I



The two observed reaction courses become intelligible if we assume that two different equilibria are established between 4-nitrobenzophenone and amide ion, one of which leads ultimately to cleavage and the other, by loss of hydride ion, to amination (see Scheme I). Such amination reactions find precedent in the behavior of various aromatic nitro compounds with alkali metal piperidides and diphenylamides[6] and with the hydroxylation of nitrobenzene by potassium hydroxide,[7] although substrate reduction is a complication in some of these reactions.

We next examined the behavior of 4-nitrodiphenyl sulfone and of 4-nitrodiphenyl sulfoxide. When 4-nitrodiphenyl sulfone in ethanol was treated with potassamide in ammonia, competitive substitution reactions occurred, leading to 4-ethoxydiphenyl sulfone and 4-ethoxynitrobenzene, with the former predominating; however, the corresponding amino compounds were produced when tetrahydrofuran was used as cosolvent. 4-Nitrodiphenyl

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(1) M. S. Gibson, S. M. Vines, and J. M. Walthew, *J. Chem. Soc., Perkin Trans. 1*, 155 (1975).

(2) J. F. Bunnett and B. F. Hrutfiord, *J. Org. Chem.*, **27**, 4152 (1962).

(3) S. Meyerson, I. Puskas, and E. K. Fields, *J. Am. Chem. Soc.*, **88**, 4974 (1966); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, CA, 1967, p 515.

(4) K. Schofield and R. S. Theobald, *J. Chem. Soc.*, 1505 (1950).

(5) A. J. Quillinan and F. Scheinmann, *J. Chem. Soc., Perkin Trans. 1*, 1329 (1973).

(6) Cf.: R. Huisgen and H. Rist, *Justus Liebigs Ann. Chem.*, **594**, 159 (1955); W. Bradley and R. Robinson, *J. Chem. Soc.*, 1254 (1932); F. E. Bergstrom, I. M. Granara, and V. Erickson, *J. Org. Chem.*, **7**, 98 (1942).

(7) A. Wohl, *Ber. Dtsch. Chem. Ges.*, **32**, 3486 (1899); A. Wohl and W. Aue, *ibid.*, **34**, 2444 (1901); German Patent 116790 (1901).

sulfoxide reacted less cleanly under these conditions to give 4-nitroaniline and diphenyl disulfide

2- and 4-Nitrotoluenes were next examined. 2-Nitrotoluene gave 2,2′-dinitrobibenzyl, and 4-nitrotoluene similarly gave 4,4′-dinitrobibenzyl, together with 4,4′-dinitrostilbene as a byproduct. The last compound was shown to arise from dehydrogenation of 4,4′-dinitrobibenzyl under similar reaction conditions. 4-Nitrotoluene has been found to give, via a radical process, 4,4′-dinitrobibenzyl on treatment with potassium *tert*-butoxide in *tert*-butyl alcohol/dimethyl sulfoxide (Me_2SO), and similar dimerizations have been noted in other basic media.[8]

We last examined the reactions of 4-nitrobenzophenone and 4-nitrodiphenyl sulfone with sodamide in ethylenediamine (EDA). This system can in principle function as the hydride source, as can ethanolic sodium or potassium ethoxide for the reduction of nitro compounds, with the anion of EDA being dehydrogenated to the labile aminoacetaldimine which is then transformed to other products. 4-Nitrobenzophenone was reduced to 4,4′-dibenzoylazobenzene with the corresponding azoxy compound as the minor product; the same product (azo compound) was also produced by conventional reduction of the nitro compound by using zinc and sodium hydroxide, again with the azoxy compound as contaminant. Isolation of the azo compound free from the azoxy compound was tedious but was eventually achieved by repeated crystallization. 4,4′-Bis(benzenesulfonyl)azobenzene was similarly obtained from 4-nitrodiphenyl sulfone and sodamide in EDA.

Experimental Section

Mass spectra were determined with an AEI MS-30 double-beam spectrometer; *m/e* values are quoted for the lowest isotopic species and relative intensities are noted where appropriate in parentheses. ^1H NMR spectra were recorded with Varian A60 and Bruker WP60 instruments (tetramethylsilane as internal standard). IR data are reported for KBr disks.

Criteria are noted in parentheses for comparisons involving authentic samples.

Aromatic nitro compounds were commercial samples except for 4-nitrodiphenyl sulfone and 4-nitrodiphenyl sulfoxide which were prepared from 4-nitrodiphenyl sulfide by standard oxidation using hydrogen peroxide. In the preparation of the sulfide from thiophenol, 4-fluoronitrobenzene, and ethanolic potassium ethoxide, we noted formation of a byproduct (bronze needles from ethanol), mp 118–119 °C.

Anal. Calcd for $C_{24}H_{18}N_2OS_2$: C, 69.56; H, 4.34; S, 15.46. Found: C, 69.33; H, 4.12; S, 15.57.

This was identified as 4,4′-bis(phenylthio)azoxybenzene (TLC and IR and mass spectra), alternatively prepared as follows. 4-Nitrodiphenyl sulfide (2.31 g, 10.0 mmol) in absolute ethanol (50 mL) was added to a stirred solution of potassium ethoxide (from 0.39 g, 10.0 mmol, of potassium) in ethanol (200 mL), and the mixture was refluxed for 15 h. When the mixture was cool, the azoxy compound (0.4 g, 0.97 mmol, 19%) was filtered off and crystallized from ethanol to give bronze needles: 0.35 g, 0.88 mmol, 17%; mp 118–119 °C; IR 1575, 1475, 1450, 830, 750, and 685 cm^{-1}; mass spectrum, *m/e* (rel intensity) 414 (M^+, 93), 398 (M – O, 25), 199 (62), 198 (56), 185 ($C_6H_5SC_6H_4$, 93), 184 (100). Concentration of the ethanolic reaction filtrate gave unreacted 4-nitrodiphenyl sulfide (1.8 g, 7.8 mmol, 78%), mp 54–55 °C.

Reactions with KNH_2/NH_3: General Procedure. Small chips of sodium were added to liquid ammonia until a permanent blue color was obtained. Ammonia was then distilled from this solution into the reaction vessel. To the distilled ammonia was then added a small chip of potassium, followed by a small crystal of ferric nitrate. The requisite amount of potassium was then added, and the mixture was then stirred until the blue color gave way to the pale grey of the potassamide solution. The nitro compound in dry tetrahydrofuran (THF) or dry ethanol was then added to the stirred solution. Quantities and reaction times are noted in parentheses. Ammonium chloride and ether were then added, and the ammonia was allowed to evaporate. Water was then added, and the crude solid product was filtered off; the aqueous filtrate was processed separately.

(a) 4-Nibrobenzophenone. 4-Nitrobenzophenone (4.26 g, 18.8 mmol) in THF (100 mL) and potassamide (from 3.9 g, 100 mmol, of potassium) in ammonia (700 mL) gave (7 h; 5 g of NH_4Cl) a brown solid A and aqueous solution B. Solid A was extracted with chloroform, the extract was evaporated, and the residue was chromatographed (Florisil/benzene). This gave 4-nitrobenzophenone (1.9 g, 8.4 mmol, 45%) followed by 3-amino-4-nitrobenzophenone (0.8 g, 3.2 mmol, 17%); several crystallizations from aqueous ethanol gave an analytical sample (0.3 g, 1.24 mmol, 7%) as pale yellow plates: mp 200–201.5 °C; ^1H NMR (Me_2SO-d_6) δ 10.87 (2 H, br s, exchangeable with D_2O), 8.3–8.0 (4 H, m), 7.9–7.6 (4 H, m); IR 3340 (NH), 1660 (C=O), 1530 and 1350 (NO_2) cm^{-1}; mass spectrum, *m/e* (rel intensity) 242 (M^+, 5), 226 (M – O, 2), 225 (M – OH, 2), 212 (M – NO, 3), 105 (C_6H_5CO, 100), 77(C_6H_5, 67).

Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.13; N, 11.57. Found: C, 64.59; H, 4.04; N, 11.57.

Nonidentity with an authentic sample of the isomeric 2-amino-4-nitrobenzophenone, mp 172–173 °C, was established by determination of the mixture melting point (147–149 °C), TLC comparisons, and comparisons of IR and mass spectra.

Solution B was acidified (HCl) and extracted with chloroform. Evaporation and crystallization from water, followed by sublimation, gave benzoic acid (0.6 g, 5.4 mmol, 31%) as plates, mp 122 °C, identical (mixture melting point, IR and mass spectra) with an authentic specimen. The residual yellow gum from the sublimation (135 mg, <0.55 mmol, 3%) was identified as 3-hydroxy-4-nitrobenzophenone but not obtained pure: ^1H NMR ($CDCl_3$) δ 10.9 (1 H, br s, exchangeable with D_2O), 9.0–8.3 (4 H, m), 7.6–7.2 (4 H, m); mass spectrum, *m/e* (rel intensity) 243 (M^+, 10), 226 (M – OH, 2), 166 (14), 105 (C_6H_5CO, 100), 77 (C_6H_5, 76).

(b) 4-Nitrodiphenyl Sulfone. (i) 4-Nitrodiphenyl sulfone (2.63 g, 10.0 mmol) in dry ethanol (75 mL) and potassamide (from 7.8 g, 200 mmol, of potassium) in ammonia (500 mL) gave (8 h; 6 g of NH_4Cl) a brown solid C and aqueous solution D. Solid C was extracted with ethanol, the extract was evaporated, and the residue was chromatographed (Florisil/benzene). This gave 4-ethoxydiphenyl sulfone, which crystallized from benzene/ethanol as plates: 1.7 g, 6.5 mmol, 65%; mp 114.5–115 °C; ^1H NMR ($CDCl_3$) δ 8.0–6.8 (9 H, m), 4.05 (2 H, q), 1.41 (3 H, t); IR 1260 (ArOR), 1325 and 1150 (S=O) cm^{-1}; mass spectrum, *m/e* (rel intensity) 262 (M^+, 100), 141 ($C_6H_5SO_2$, 55).

Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.11; H, 5.34. Found: C, 63.99; H, 5.34.

Further elution gave 4-ethoxynitrobenzene which crystallized from ethanol as yellow prisms: 0.49 g, 2.9 mmol, 29%; mp 56–60 °C (lit.[9] mp 60 °C); ^1H NMR ($CDCl_3$) δ 8.13 (A) and 6.89 (B) (4 H, A_2B_2 q), 4.11 (2 H, q), 1.42 (3 H, t); IR 1265 (ArOR), 1510, 1350 (NO_2), 1175 and 810 (1,4-disubstituted benzene) cm^{-1}; mass spectrum, *m/e* (rel (rel intensity) 167 (M^+, 100), 151 (M – O, 5), 139 (M – C_2H_4, 54), 123 (5), 109 (52).

(ii) 4-Nitrodiphenyl sulfone (2.63 g, 10 mmol) in THF (50 mL) and potassamide (from 3.9 g, 100 mmol, of potassium) in ammonia (500 mL) gave (5 h; 5 g of NH_4Cl) a brown solid E and aqueous solution F. Solid E was chromatographed (Florisil/benzene) to give 4-aminodiphenyl sulfone, which crystallized from benzene/ethanol as needles (256 mg, 1.1 mmol, 11%), mp 176 °C (lit.[10] mp 176 °C).

An authentic sample of 4-aminodiphenyl sulfone (85% yield) was prepared for comparison by reduction of 4-nitrodiphenyl sulfone (1.0 g, 3.8 mmol) using the method of Balcom and Furst (hydrazine hydrate/ethanol/Raney Ni):[11] mp 175–176 °C; IR 3450 (NH), 3375, 3250, 1650, 1330, 1150 (S=O) cm^{-1}; mass spectrum, *m/e* (rel intensity) 233 (M^+, 96), 141 ($C_6H_5SO_2$, 17).

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(8) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **89**, 300 (1967), and references cited.

(9) D. H. Richardson, *J. Chem. Soc.*, 522 (1926); A. C. Roy and T. N. Ghosh, *J. Indian Chem. Soc.*, **22**, 283 (1945).

(10) W. R. Waldron and E. E. Reid, *J. Am. Chem. Soc.*, **45**, 2406 (1923).

(11) D. Balcom and A. Furst, *J. Am. Chem. Soc.*, **73**, 4334 (1951).

Further elution gave 4-nitroaniline (97 mg, 0.7 mmol, 7%; mp 145 °C) identical with an authentic sample (mixture melting point, TLC, IR and mass spectra).

The aqueous solution F was extracted with ether to give a yellow solid (267 mg) which contained 4-aminodiphenyl sulfone and 4-nitroaniline (TLC, mass spectrum); this was not separated.

(c) 4-Nitrodiphenyl Sulfoxide. 4-Nitrodiphenyl sulfoxide (1.0 g, 4.04 mmol) in THF (25 mL) and potassamide (from 630 mg, 16.6 mmol, of potassium) in ammonia (200 mL) gave (3 h; 6 g of NH_4Cl) a black solid G and an aqueous solution H. Solid G was extracted with ether, and the ether solution was evaporated to give a gum which solidified on trituration with petroleum ether; this solid (80 mg) proved to be 4-nitroaniline (see later). Evaporation of the petroleum ether filtrate gave diphenyl disulfide: 125 mg, 0.58 mmol, 14%; mp and mmp 55–57 °C; the mass spectrum showed m/e 218 (M^+) and trace impurity at m/e 250.

The aqueous solution H was extracted with dichloromethane. Evaporation of the dichloromethane solution gave a gum which crystallized from ether/petroleum ether to give 4-nitroaniline (60 mg). Total recovery of 4-nitroaniline was 140 mg (1.0 mmol, 25%), mp 139–141 °C, identical with an authentic sample (mixture melting point, TLC, IR ^1H NMR, and mass spectra).

(d) 2-Nitrotoluene. 2-Nitrotoluene (2.75 g, 20.0 mmol) in THF (50 mL) and potassamide (from 11.7 g, 300 mmol, of potassium) in ammonia (650 mL) gave (12 h; 10 g of NH_4Cl) a yellow solid I and an aqueous solution. Solid I crystallized from chloroform to give 2,2′-dinitrobibenzyl (2.2 g, 8.0 mmol, 80%) as yellow prisms: mp 119–120 °C (lit.[12] mp 122 °C); ^1H NMR ($CDCl_3$) δ 8.07–7.85 (2 H, m), 7.55–7.3 (6 H, m), 3.25 (4 H, s); IR 2920 (CH), 1530 and 1345 (NO_2) cm^{-1}; mass spectrum, m/e (rel intensity) 272 (M^+, 1), 255 (M – OH, 7), 136 ($NO_2C_6H_4CH_2$, 100), 120 (66).

Anal. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.78. Found: C, 61.76; H, 4.79.

(e) 4-Nitrotoluene. 4-Nitrotoluene (2.75 g, 20.0 mmol) in THF (50 mL) and potassamide (from 2.34 g, 60.0 mmol, of potassium) in ammonia (400 mL) gave (4 h; 6 g of NH_4Cl) a brown solid J and an aqueous solution. Solid J was extracted with hot acetic acid and filtered, leaving a yellow residue (400 mg, 1.46 mmol, 15%) of 4,4′-dinitrostilbene. The acidic solution was diluted with water, and the solid (2.2 g, 8.0 mmol, 80%) was filtered off, dried, and crystallized from benzene to give 4,4′-dinitrobibenzyl as yellow needles: 2.1 g, 7.7 mmol, 77%; mp 178.5–180 °C (lit.[8] mp 179.5–180.5 °C); ^1H NMR ($CDCl_3$) δ 8.16 (A) and 6.3 (B) (8 H, A_2B_2 q), 3.0 (4 H, s); IR 2920 (CH), 1500 and 1335 (NO_2) cm^{-1}; mass spectrum, m/e (rel intensity) 272 (M^+, 50), 256 (M – O, 7), 136 ($NO_2C_6H_4CH_2$, 100), 120 (17).

A sample of 4,4′-dinitrostilbene, recrystallized from ethanol, had mp 292–293 °C (lit.[13] mp 294–295 °C) and was identical with the sample prepared in f below (mixture melting point, TLC, mass spectrum).

(f) 4,4′-Dinitrobibenzyl. 4,4′-Dinitrobibenzyl (2.2 g, 8.1 mmol) in THF (50 mL) and potassamide (from 5.5 g, 141 mmol, of potassium) in ammonia (700 mL) gave (4 h; 5 g of NH_4Cl) a yellow solid K and an aqueous solution. Solid K crystallized from ethanol to give 4,4′-dinitrostilbene: 1.6 g, 5.9 mmol, 73%; mp 292–293 °C; mass spectrum, m/e (rel intensity) 270 (M^+, 32), 254 (M – O, 5), 240 (M – NO, 31), 210 (M – 2 – NO, 100).

Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.70; N, 10.37. Found: C, 61.93; H, 3.64; N, 10.20.

Concentration of the ethanolic mother liquor gave a further crop of 4,4′-dinitrostilbene (0.6 g, 2.2 mmol, 27%), slightly contaminated with 4,4′-dinitrobibenzyl.

Reactions with $NaNH_2$ in EDA: General Procedure. The nitro compound in dry, freshly distilled EDA was added to a mixture of sodamide and EDA which had been previously stirred for 30 min under nitrogen. The mixture was stirred under nitrogen at room temperature (reaction times in parentheses), poured into iced water, and extracted with ether. After drying and evaporation of the ether, the crude product was processed as noted.

(a) 4-Nitrobenzophenone. Treatment of 4-nitrobenzophenone (1.0 g, 4.4 mmol) in EDA (20 mL) with sodamide (600 mg, 15.4 mmol) in EDA (40 mL) gave (40 h) a gummy solid which solidified (250 mg, 0.64 mmol, 29%) on trituration with petroleum ether. Crystallization from acetone gave light brown plates, mp 205–208 °C, of 4,4′-dibenzoylazobenzene (m/e 390, M^+) contaminated with the azoxy compound (m/e 406, M^+). Repeated crystallization raised the melting point to 220–221 °C. This sample was identical with that prepared as described below.

Anal. Calcd for $C_{26}H_{18}N_2O_2$: N, 7.17; mol wt, 390.13670. Found N, 7.21; mol wt (mass spectrometry), 390.11786.

The petroleum ether filtrate apparently contained 4-nitrobenzophenone and 3-amino-4-nitrobenzophenone (TLC).

The azo compound was alternatively prepared in the following way. Zinc powder (2.3 g, 35 mmol) was added to a stirred mixture of 4-nitrobenzophenone (4.0 g, 17.6 mmol) in methanol (80 mL) and sodium hydroxide (2.8 g, 70 mmol) in water (7 mL). The mixture was refluxed for 8 h, during which time a yellow solid separated out. The mixture was filtered while hot and the filter cake was washed with hot methanol (50 mL), leaving a pale yellow solid (1.3 g, 3.3 mmol, 38%), mp 205–208 °C. Like the first crystallized product from the foregoing reaction, this showed only one spot on TLC and proved to be 4,4′-dibenzoylazobenzene (m/e 390, M^+) contaminated with the azoxy compound (m/e 406, M^+); the methanol washings showed two spots on TLC, one of which was identical with that for the azo compound. Recrystallization (ethanol) gave the same azo compound as above: ^1H NMR ($CDCl_3$) δ 8.0 (s), 7.9–7.4 (m); IR 1660 (C=O), 1580 (N=N) cm^{-1}; mass spectrum, m/e (rel intensity) 390 (M^+, 25), 209 (M – $C_{13}H_9O$, 4), 181 ($C_{13}H_9O$, 100), 105 (C_6H_5CO, 62).

(b) 4′-Nitrodiphenyl Sulfone. Treatment of 4-nitrodiphenyl sulfone (1.0 g, 3.8 mmol) in EDA (25 mL) with sodamide (700 mg, 18.0 mmol) in EDA (50 mL) gave (30 h) a gum (100 mg, 0.22 mmol, 8%) which crystallized from benzene to give light brown plates, mp 275–278 °C, of 4,4′-bis(benzenesulfonyl)azobenzene; IR 1590 (N=N), 1325, 1165 and 1150 (S=O) cm^{-1}; mass spectrum, m/e (rel intensity) 462 (M^+, 33), 245 (M – $C_{12}H_9SO_2$, 8), 217 ($C_{12}H_9SO_2$, 100), 141 ($C_6H_5SO_2$, 13), 125 (C_6H_5SO, 17).

Anal. Calcd for $C_{24}H_{18}N_2O_4S_2$: N, 6.08; mol wt, 462.07087. Found: N, 6.16; mol wt (mass spectrometry), 462.06464.

Acknowledgment. We wish to thank Professor K. Schofield (University of Exeter, England) for a sample of 2-amino-4-nitrobenzophenone and the National Research Council of Canada for financial support.

Registry No. 4,4′-Bis(phenylthio)azoxybenzene, 5333-73-3; 4-nitrodiphenyl sulfide, 1223-31-0; 4-nitrobenzophenone, 1144-74-7; 3-amino-4-nitrobenzophenone, 39070-69-4; benzoic acid, 65-85-0; 4-nitrodiphenyl sulfone, 1146-39-0; 4-ethoxydiphenyl sulfone, 14193-13-6; 4-ethoxynitrobenzene, 100-29-8; 4-aminodiphenyl sulfone, 7019-01-4; 4-nitroaniline, 100-01-6; 4-nitrodiphenyl sulfoxide, 955-45-3; diphenyl disulfide, 882-33-7; 2-nitrotoluene, 88-72-2; 2,2′-dinitrobibenzyl, 16968-19-7; 4-nitrotoluene, 99-99-0; 4,4′-dinitrostilbene, 2501-02-2; 4,4′-dinitrobibenzyl, 736-30-1; 4,4′-dibenzoylazobenzene, 19617-86-8; 4,4′-bis(benzenesulfonyl)azobenzene, 71819-33-5; potassamide, 17242-52-3; sodamide, 7782-92-5.

Reinvestigation of the Reaction of Ethyl Acetoacetate with Styrene Oxide

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Adams and VanderWerf[2] have reported that the reaction of ethyl acetoacetate with styrene oxide gives α-acetyl-γ-phenyl-γ-butyrolactone (1) as the sole product. Subse-

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(12) M. Busch and B. Weiss, *Ber. Dtsch. Chem. Ges.*, **33**, 2709 (1900).

(13) P. L'Ecuyer, F. Turcotte, J. Giguere, C. A. Olivier, and P. Roberge, *Can. J. Res., Sect. B*, **26**, 70 (1948).

(1) Present address: Monsanto Agricultural Products Co., St. Louis, Mo. 63166.

(2) R. M. Adams and C. A. VanderWerf, *J. Am. Chem. Soc.*, **72**, 4368 (1950).