**Benzildianil (3a).**—In a 50-ml erlenmeyer flask was placed 3.62 g (0.02 mol) of *N*-benzylideneaniline (**1a**) in 30 ml of dry DMSO. To this solution was added 0.98 g (0.02 mol) of powdered sodium cyanide, and the flask was stoppered and magnetically stirred for a period of 72 hr at room temperature (20°). The reaction mixture was poured slowly, with stirring into an ice-water mixture and the precipitated product was filtered. The crude yield was 3.6 g, mp 107–130°. This was taken up in 20 ml of boiling benzene, diluted with 5 ml of petroleum ether, and allowed to cool. A little benzanilide separated and was filtered; the filtrate was evaporated to half its volume and 5 ml of boiling ethanol was then added. On cooling, 2.45 g of dianil **3a** separated out as light yellow plates, mp 142–143°. Further evaporation of filtrate and cooling afforded an additional 0.7 g of dianil **3a**, mp 139–141°. A very pure sample of dianil **3a**, mp 144–145°, was obtained by recrystallization from petroleum ether: uv $\lambda_{max}$ (ethanol) 264 nm ($\epsilon$ 37,350); ir 1620 cm$^{-1}$ (C=N) ($CHCl_3$).

The above reaction when run in DMF gave no benzanilide; dianil **3a** was isolated in 77% yield.

In general, the reaction of aldimines **1** with cyanide ion in DMSO or DMF was carried out at room temperature for a period of 72 hr. No care was taken to exclude air from the reaction. The reaction mixture was poured in ice-water and the crude product was crystallized to afford $\alpha$ diketimines **3b–3l**. Their melting points and analytical data are summarized in Table II.

**Benzil (4a).**—A mixture of 1 g of dianil **3a** and 10 ml of concentrated hydrochloric acid was magnetically stirred for 14 hr. The precipitated diketone **4a** was filtered, mp 94–95° (0.63 g, 92%).

Diketones **4b–4l** were prepared in the same fashion as described for **4a**. Their melting point data are recorded in Table II.

**Registry No.**—**1j**, 32349-41-0; **1k**, 27738-39-2; **1l**, 32349-43-2; **3a**, 7510-33-0; **3b**, 21854-87-5; **3c**, 21854-89-7; **3d**, 21854-88-6; **3e**, 21913-95-1; **3f**, 32349-49-8; **3g**, 24099-56-7; **3h**, 32349-50-1; **3i**, 32382-35-7; **3j**, 32349-51-2; **3k**, 24099-55-6; **3l**, 32349-53-4.

**Acknowledgments.**—We thank the Research Corporation (New York) and the Academic Grant Fund of Loyola University, New Orleans, for support and Mr. Chris Christensen for valuable assistance.

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# Preparation of *N*,*N*-Dialkyl Aromatic Amines *via* Benzyne Reaction[1a]

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*Received June 1, 1971*

This paper reports on the investigation of the reaction of haloaromatic compounds with sodamide in secondary aliphatic amine solvents. Two factors prompted this study. First, Bunnett and Brotherton[2] proposed a distinct steric interaction in the preparation of certain *N*,*N*-dialkylanilines *via* the reaction of bromobenzene and sodamide in refluxing secondary amine solvent. Thus, *N*,*N*-diethylaniline was prepared in only a 53% yield after 2 hr of heating. Heating for 16 hr increased the yield to only 64%. In contrast, we[3] have shown that *N*-alkylanilines are readily obtained by the action of bromobenzene and sodamide in primary aliphatic amine solvent at room temperature. Steric factors were of minor importance in this system since good yields of amines containing bulky groups such as *tert*-butyl (72%) are achieved. Higher yields of *N*-alkylanilines were precluded by further addition of *N*-alkylaniline ion to benzyne forming *N*-alkyl-*N*-phenylanilines. This indicated that the extent of those steric effects proposed by Bunnett in the addition of secondary amines to benzyne might be in error. In support of this conclusion, Caubere and Derozier[4] observed that good yields of *N*,*N*-dialkylanilines were obtained if bromobenzene and the appropriate dialkylamine were allowed to react in the presence of sodamide and sodium *tert*-butoxide in tetrahydrofuran. Thus, it was clear that a reinvestigation of the reaction of bromobenzene and sodamide in secondary aliphatic amine solvents was in order.

Secondly, it is well established that certain substituted haloaromatic compounds are in part reductively dehalogenated by treatment with certain alkali dialkylamides.[5] For example, Benkeser[6] has noted that the reaction of lithium dimethylamide with *o*-bromoanisole afforded anisole (17%) in addition to the expected benzyne product, *N*,*N*-dimethyl-*m*-anisidine (35%). Interestingly, we[7] have shown that competition reactions between acetonitrile anion and dimethylamine for various arynes (including 3-methoxybenzyne) generated by the action of sodamide on the corresponding haloaromatic compound produced no reduced dehalogenated compounds. In addition, high yields of several meta derivatives of *N*-alkylanilines were obtained by the reaction of sodamide and various primary aliphatic amines with ortho-substituted haloaromatic compounds possessing strong −I groups [$OCH_3$, Cl, and $N(CH_3)_2$].[8] No reductive dehalogenated products were observed in any case. Therefore, it was of interest to see if high yields of meta derivatives of *N*,*N*-dialkylanilines could also be obtained using sodamide. Also, more insight into the nature of the reduction mechanism would be obtained.

## Experimental Section

Glpc analyses were performed on a MicroTek instrument Model GC 1600 using helium as the carrier gas at a flow rate of 45 ml/min, inlet and detector temperatures at 250°, and a 10 ft × 0.125 in. i.d. column packed with 5% Carbowax, 20M (polyethylene oxide) on Chromosorb W, acid-washed, 60–80 mesh. Microanalytical analyses were performed by Chemalytics, Tempe, Ariz.

**Starting Materials.**—Reagent grade sodium was obtained from J. T. Baker. Amine solvents, obtained from Aldrich Co., were dried over anhydrous calcium hydride for 24 hr and then distilled directly into a thoroughly dried reaction flask. Bromobenzene and *o*-bromoanisole, which were obtained from Eastman Kodak, were dried over calcium chloride and distilled before use. *o*-Chloro-*N*,*N*-dimethylaniline was prepared by the method of Huenig.[9]

**General Procedure.**—The reactions were carried out in a manner similar to that previously described[8] with the exception that sodamide was prepared *in situ* by the addition of sodium to liquid ammonia in the presence of ferric nitrate. In addition, the mole ratio of 0.3:0.1 sodamide to haloaromatic in 100 ml of amine

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(1) (a) Supported in part by Grant N-118 from the Robert A. Welch Foundation, Houston, Tex. (b) Robert A. Welch Predoctoral Fellow.

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TABLE I

PREPARATION OF *N*,*N*-DIALKYLANILINES, G–$C_6H_4NR_2$

| G | R | Registry no. | Yield, % | Bp, °C (mm) | Formula | | C, % | H, % | N, % |
|---|---|---|---|---|---|---|---|---|---|
| H | $C_2H_5$ | | 93 | 77 (7)[a] | | | | | |
| | $i$-$C_3H_7$ | | 22[b] | 87 (9)[c] | | | | | |
| | $n$-$C_3H_7$ | | 88 | 118 (5)[d] | | | | | |
| | $n$-$C_4H_9$ | | 74 | 89 (0.8)[e] | | | | | |
| | $i$-$C_4H_9$ | | 81 | 107 (4)[f] | | | | | |
| $m$-$OCH_3$ | $C_2H_5$ | | 95 | 100–102 (1.2)[g] | | | | | |
| | $i$-$C_3H_7$ | 7000-87-5 | 72 | 101–103 (1.2) | $C_{13}H_{21}NO$ | Calcd | 75.32 | 10.21 | 6.76 |
| | | | | | | Found | 75.45 | 10.36 | 7.05 |
| | $n$-$C_4H_9$ | | 78 | 134–135 (1.0)[h] | | | | | |
| | $i$-$C_4H_9$ | 32319-29-2 | 65 | 118–120 (1.1) | $C_{14}H_{23}NO$ | Calcd | 76.58 | 10.71 | 5.95 |
| | | | | | | Found | 76.43 | 10.65 | 6.04 |
| $m$-$N(CH_3)_2$ | $C_2H_5$ | | 95 | 125–128 (1.9)[i] | | | | | |
| | $i$-$C_3H_7$ | 32319-30-5 | 38 | 105–107 (1.1) | $C_{14}H_{24}N_2$ | Calcd | 76.63 | 10.98 | 12.71 |
| | | | | | | Found | 76.82 | 10.80 | 12.53 |
| | $n$-$C_4H_9$ | 32319-31-6 | 87 | 138–140 (1.3) | $C_{15}H_{26}N_2$ | Calcd | 77.36 | 11.36 | 11.28 |
| | | | | | | Found | 78.42 | 11.41 | 11.46 |
| | $i$-$C_4H_9$ | 32319-32-7 | 82 | 124–126 (1.0) | | Found | 77.32 | 11.54 | 11.27 |

[a] Lit.[2] bp 62–66° (3 mm). [b] Yield was increased to 38% by using reaction time of 6 hr. [c] Lit.[2] bp 95.5° (12 mm). [d] Lit.[10] bp 110–115° (10 mm). [e] Lit.[2] bp 103.5–106° (3.5 mm). [f] Lit.[11] bp 146° (21 mm). [g] Lit.[12] bp 87–89° (0.5 mm). [h] Lit.[12] bp 136.5–138.5° (1.9 mm). [i] Lit.[13] bp 100–102° (0.5 mm).

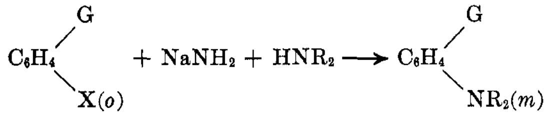
solvent, and a reaction time of 3 hr (after color change) was utilized. Products were obtained by vacuum distillation. Vpc analysis revealed that the small amounts (less than 5%) of ortho isomers were readily removed from the desired meta-substituted *N*,*N*-alkylaniline by one distillation. Pertinent data are listed in Table I.

## Results and Discussion

Table I[2,10–13] reveals that in general good to excellent yields of *N*,*N*-dialkylanilines are obtained when bromobenzene is allowed to react with sodamide in various secondary amine solvents. Improved yields in the case of *N*,*N*-diethylaniline (93% *vs.* 53%[2]) is most likely attributable to our use of an improved amine drying procedure (drying over $CaH_2$ for 24 hr *vs.* azeotropic benzene distillation.) It should be pointed out that diethylamine is very difficult to dry. The high yield of *N*,*N*-diethylaniline reported in this study was obtained only when an extensive drying period was utilized. The low yield (22%) of *N*,*N*-diisopropylaniline observed in this study, however, is the same as that obtained by Bunnett[2] indicating that at least in this system steric effects are important. Huisgen[14] has observed a similar effect in the nucleophilic addition to 1-naphthyne. In that study steric effects only became important when the attacking secondary amine possessed a carbon atom ($\alpha$ to the nitrogen atom) substituted with at least two alkyl groups. The yields obtained in this study compare very favorably with those obtained by Caubere and Derozier,[4] indicating that no synthetic advantage is obtained by employing both sodium amide and sodium *tert*-butoxide.

$$C_6H_5Br + NaNH_2 + R_2NH \longrightarrow C_6H_5NR_2$$
$$R = C_2H_5,\ i\text{-}C_3H_7,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ i\text{-}C_4H_9$$

Table I also indicates that, in general, good to excellent yields of *N*,*N*-dialkyl-*m*-anisidines (95–65%) and *N*,*N*-dialkyl-*N′*,*N′*-dimethylphenylenediamines (95–38%) are produced by the reaction of the corresponding ortho-substituted haloaromatic compounds with sodamide in various secondary amine solvents. Only in the case of the reaction between diisopropylamine and *o*-chloro-*N*,*N*-dimethylaniline were low yields (38%) achieved.



$$C_6H_4(G)X(o) + NaNH_2 + HNR_2 \longrightarrow C_6H_4(G)NR_2(m)$$

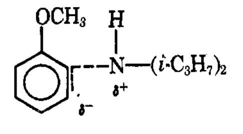
G = $OCH_3$, $N(CH_3)_2$
X = Cl, Br

R = $C_2H_5$, $i$-$C_3H_7$,
$n$-$C_4H_9$, $i$-$C_4H_9$

The generally good to high yields are due in part to the fact that no reductive dehalogenated products (anisole and *N*,*N*-dimethylanilines) are formed. Although there is still controversy[15,16] over the reduction mechanism, it is generally agreed that alkali dialkylamides possessing $\alpha$-hydrogen atoms are the hydride ion donors. Experimentally, no liberation of ammonia was observed until the addition of the haloaromatic compound. Consequently, no appreciable amount of the dialkylamine was converted to the corresponding sodium dialkylamide. Thus, the reduction pathway was circumvented.

$$R_2NH + NaNH_2 \longrightarrow R_2NNa + NH_3$$

Interestingly, the steric effects operating on the addition of diisopropyl amine to 3-methoxybenzyne are considerably less than those observed in the addition of the same amine to 3-(*N*,*N*-dimethylamino)benzyne. It is known that 3-methoxy groups destabilize arynes.[7] Hence, the low steric requirements in the diisopropylamine addition to 3-methoxybenzyne simply reflects the longer carbon–nitrogen bond-making length in the transition state for this particular nucleophilic addition.



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