Experimental Section

Proton magnetic resonance spectra were obtained with a Varian HA-100 nmr spectrometer or with a Varian A-56/60A spectrometer equipped with a Varian C-1024 time-averaging computer. The probe on the A-56/60A spectrometer carried a dewar-jacketed probe insert which could maintain stable temperatures as low as −100°, so that low-temperature, time-averaged spectra could be obtained with no great difficulties.

The starting halides were commercial products and used as received. Tetrahydrofuran (Matheson Coleman and Bell) was distilled from lithium aluminum hydride and stored over Linde 13X molecular sieves. Solvent was never stored for more than 3 days. *N,N,N′,N′*-tetramethylethylenediamine (Matheson Coleman and Bell) was dried over potassium hydroxide and then distilled from sodium immediately before adding to Grignard reagents. Magnesium was in the form of shavings ground from blocks of triply sublimed magnesium.[11] Dioxane (Eastman) was distilled from lithium aluminum hydride before use.

The various alkylmagnesium reagents were prepared directly in sealed nmr tubes. After centrifugation of solids to one end, careful decantation of the liquid to the other end of the tube provided a clear sample suitable for nmr spectroscopy.

Registry No.—*N,N,N′,N′*-Tetramethylethylenediamine, 110-18-9; ethylmagnesium bromide, 925-90-6; diethylmagnesium, 557-18-6; magnesium bromide, 7789-48-2.

[11] We thank Dow Chemical Co. for the gift of magnesium.

A Convenient Route to Aromatic α Diketimines and α Diketones

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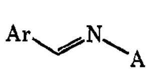
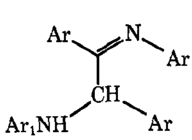
In a preliminary report[1] we have described a simple cyanide ion catalyzed oxidative dimerization of some aromatic aldimines **1** to α diketimines **3**.[2] This paper gives details of these experiments and additional examples delineating to some extent the scope and limitations of this method. Further, the smooth acid hydrolysis of α diketimines **3** constitutes a convenient route to α diketones **4**. Since the appearance of our communication another report of the cyanide ion catalyzed dimerization of aromatic Schiff bases has appeared.[3]



1



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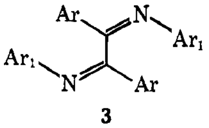

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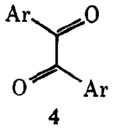
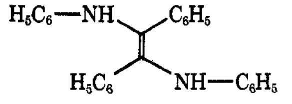


4

Although the benzoin condensation[4] is usually carried out in alcoholic solvents, we decided to investigate the reaction of aromatic aldimines **1** with cyanide ion in dimethyl sulfoxide (DMSO) in the hope that the initially formed anilinoimines **2**, a formal benzoin type condensation product of **1**, would suffer *in situ* oxidation by DMSO to yield directly diketimines **3**. We were gratified to find that the reaction of a 0.66 *M* solution of *N*-benzylideneaniline (**1a**) in dry DMSO with an equivalent amount of sodium cyanide at 20° afforded benzildianil (**3a**) in 65% yield. A recent note[3] describes the formation of dianilinostilbene (**5**) in dimethylformamide (DMF) when the reaction is run under nitrogen. Apparently under our conditions the initial product (**5** or **2a**) undergoes aerial oxidation to diketimine **3a**. We also find that the oxidative dimerization of **1** to **3** proceeds as well or better in DMF. The role of DMSO in this reaction is therefore only as a solvent (and not additionally as an oxidizing agent).

The data for the reaction carried out with 0.6–0.7 *M* solutions of **1** is presented in Table I. A small amount of anilide **6** was usually a by-product of reactions run in DMSO. The ratio of α diketimines **3** to anilide **6** was sensitive to both concentrations of azomethine **1** and to temperature (see Table I). The best results were obtained by running the reaction in dilute solution using DMF as solvent.



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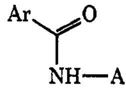

6

That the cyanide ion acts as a specific catalyst in the oxidative dimerization **1** to **3** is shown by the observations that transformation of **1a** to **3a** proceeds to completion with as little as 0.1 molar equiv of cyanide ion, and **1a** in DMSO or DMF was unchanged either alone or in the presence of sodium hydroxide. The possibility of the reaction proceeding *via* prior hydrolytic cleavage of **1a** to benzaldehyde and aniline is dismissed, since the reaction of benzaldehyde, aniline, and cyanide ion in DMSO gives only benzoin.

Inspection of Table I shows that this method for the synthesis of α diketimines **3** is fairly general and the substituents in Ar and Ar₁ can vary considerably. The reaction is apparently limited to aromatic aldimines. However, diketimines were not obtained from *p*-dimethylaminobenzylideneaniline (**1m**), *p*-hydroxybenzylideneaniline (**1n**), *p*-nitrobenzylideneaniline (**1p**), *o*-methoxybenzylideneaniline (**1q**), or benzylidenecyclohexylamine (**1r**); the benzoin condensation also fails with the aromatic aldehydes of **1m**, **1n**, or **1p**.

The mechanism of this reaction appears to resemble that of the benzoin condensation;[5] a possible route is presented in Scheme I.

Experimental Section

General.—Melting points were taken on a Thomas–Hoover melting point apparatus and are uncorrected. Analyses were

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[1] J. S. Walia, J. Singh, M. S. Chattha, and M. Satyanarayana, *Tetrahedron Lett.*, 195 (1969).

[2] For synthesis of ketimines, see (a) R. W. Layer, *Chem. Rev.*, **63**, 489 (1963); (b) H. Weingarten, J. P. Chupp, and W. A. White, *J. Org. Chem.*, **32**, 3246 (1967); (c) J. S. Walia, L. Heindl, H. Lader, and P. S. Walia, *Chem. Ind. (London)*, 155 (1968); (d) R. Patarcity and B. R. Franko-Filipasic, *ibid.*, 1704 (1969); (e) S. Dayagi and Y. Degani in "The Chemistry of Carbon–Nitrogen Double Bond," S. Patai. Ed., Interscience, New York, N. Y., 1970, Chapter 2.

[3] H.-D. Becker, *J. Org. Chem.*, **35**, 2099 (1970).

[4] W. S. Ide and J. S. Buck in "Organic Reactions," Vol. IV, R. Adams, Ed., Wiley, New York, N. Y., 1948, p 269.

[5] R. L. Schowen, J. P. Kuebrich, M.-S. Wang, and M. E. Lupes, *J. Amer. Chem. Soc.*, **93**, 1214 (1971).

Table I

Yields of α Diketimines, Anilides, and α Diketones

Run	Ar	Ar₁	Solvent	Yield, %		
				diketimine **3**	anilide **6**	diketone **4**
a	Phenyl	Phenyl	DMSO	65	6	92
	Phenyl	Phenyl	DMF	77		
	Phenyl	Phenyl	DMSO[a]	48	41	
	Phenyl	Phenyl	DMSO[b]	75		
b	*p*-Chlorophenyl	Phenyl	DMSO	58	11	90
	p-Chlorophenyl	Phenyl	DMSO[a]	41	29	
	p-Chlorophenyl	Phenyl	DMSO[b]	65	6	
c	*p*-Methoxyphenyl	Phenyl	DMSO	59	4	98
	p-Methoxyphenyl	Phenyl	DMSO[a]	60	14	
	p-Methoxyphenyl	Phenyl	DMSO[b]	72	1	
d	*p*-Methylphenyl	Phenyl	DMSO	72		92
e	*o*-Chlorophenyl	Phenyl	DMSO	83		96
f	Phenyl	*p*-Methoxyphenyl	DMSO	50	1–2	90
g	Phenyl	*p*-Methylphenyl	DMF	60		91
h	Phenyl	*m*-Methoxyphenyl	DMF	54		95
i	Phenyl	*p*-Chlorophenyl	DMSO	73	10	87
j	3,4,5-Trimethoxyphenyl	Phenyl	DMF	65		93
k	3,4-Methylenedioxyphenyl	Phenyl	DMF	28		92
l	Phenyl	3,4-Dimethyl-5-isoxazyl	DMF	36		86

[a] At 59–60°. [b] Using 0.13 *M* solution.

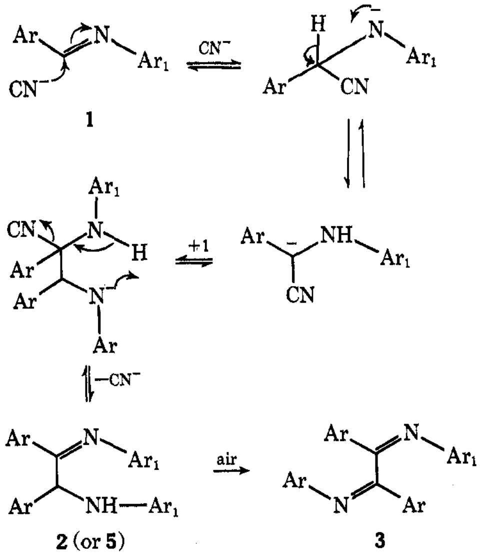
Table II

Melting Points and Characterizations of Diketimines, Diketones, and Anilides

Run	Diketimine **3**							Diketone **4**		Anilide **6**	
		Calcd, %			Found, %						
	Mp, °C	C	H	N	C	H	N	Mp, °C	Lit. mp, °C	Mp, °C	Lit. mp, °C
a	144–145[a]	86.66	5.55	7.73	86.31	5.72	7.84	94–95	94–95[b]	160–161	162[c]
b	155–156	72.73	4.20	6.52	72.47	4.36	6.22	198–200	200[d]	194–196	194[e]
c	150–151	80.00	5.71	6.67	79.58	5.56	6.49	131–133	131–132[f]	170–171	168–169[g]
d	147–148	86.56	6.23	7.21	86.30	6.35	7.39	104–105	104–105[h]	*i*	
e	216–217	72.73	4.20	6.52	72.88	4.43	6.75	133–134	133–134[j]	*i*	
f	162–163	80.00	5.71	6.67	80.11	5.70		94–95	94–95[b]	153–154	156[k]
g	157–158	86.56	6.23	7.21	86.23	6.15		94–95	94–95[b]	*i*	
h	134–135	80.00	5.71	6.67	79.81	5.80		94–95	94–95[b]	*i*	
i	172–173	72.73	4.20	6.52	72.63	4.27	6.53	94–95	94–95[b]	192–194	192–193[l]
j	120–121	71.06	5.97	5.18	70.52	6.29		191–192	192–193[m]	*i*	
k	125–127	74.96	4.49	6.25	74.81	4.33		170–171	170–171[n]	*i*	
l	223–224	72.34	5.32	14.05	72.41	5.57		94–95	94–95[b]	*i*	

[a] Lit. mp 141–142: G. Reddelien, *Chem. Ber.*, **46,** 2723 (1913). [b] I. A. Pearl and W. M. Dehn, *J. Amer. Chem. Soc.*, **60,** 57 (1938). [c] H. Franzen, *Chem. Ber.*, **42,** 2466 (1909). [d] A. Hantzsch and W. H. Glower, *ibid.*, **40,** 1519 (1907). [e] A. Hantzsch, *ibid.*, **24,** 56 (1891). [f] C. Deliwala and S. Rajgopalan, *Proc. Indian Acad. Sci.*, **31A,** 107 (1950). [g] R. Haller, *C. R. Acad. Sci.*, **121,** 190 (1895). [h] D. Vorlander, *Chem. Ber.*, **46,** 2455 (1911). [i] Not obtained. [j] Reference *f*. [k] F. Reverdin, *Chem. Ber.*, **42,** 1523 (1909). [l] R. von Walther, *J. Prakt. Chem.*, [2] **67,** 453 (1903). [m] I. A. Pearl, *J. Org. Chem.*, **22,** 1229 (1957). [n] C. D. Shacklett and H. A. Smith, *J. Amer. Chem. Soc.*, **75,** 2654 (1953).

Scheme I



performed by Drs. Weiler and Strauss, Microanalytical Laboratories, Oxford, England. DMSO and DMF were distilled over CaH_2 *in vacuo* and stored over molecular sieves.

Starting Material.—*N*-Benzylideneaniline (**1a**) was commercially available and was used without further purification. The *N*-benzylideneaniline derivatives **1b–1i** were prepared by standard procedures, mostly following the method of Law.[6]

***N*-3,4,5-Trimethoxybenzylideneaniline** (**1j**).—Faint yellow crystals were recrystallized from benzene–petroleum ether (bp 30–60°), mp 84–85°.

Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 70.56; H, 6.13.

***N*-3,4-Methylenedioxybenzylideneaniline** (**1k**).—Light, pale crystals were recrystallized from benzene–petroleum ether, mp 63–64°.

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92. Found: C, 74.44; H, 4.89.

***N*-Benzylidene-3,4-dimethylisoxazylamine** (**1l**).—Colorless crystals were recrystallized from petroleum ether–benzene, mp 90–91°.

Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04. Found: C, 72.10; H, 5.81.

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[6] H. D. Law, *J. Chem. Soc.*, **101,** 154 (1912).

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 λ_{max} (ethanol) 264 nm (ϵ 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 α 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.

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

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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.

[2] J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **22**, 832 (1957).

[3] E. R. Biehl, S. M. Smith, and P. C. Reeves, *ibid.*, **36**, 1841 (1971).

[4] P. Caubere and N. Derozier, *Bull. Soc. Chim. Fr.*, 1737 (1969).

[5] For a comprehensive listing see R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, pp 101–105.

[6] R. A. Benkeser and C. E. DeBoer, *J. Org. Chem.*, **21**, 365 (1956).

[7] E. R. Biehl, E. Nieh, and K. C. Hsu, *ibid.*, **34**, 3595 (1969).

[8] E. R. Biehl, R. Patrizi, and P. C. Reeves, *ibid.*, **36**, 3252 (1971).

[9] S. Huenig, *Chem. Ber.*, **85**, 1056 (1952).