Ethyl *N*-Carbethoxypropioimidate.—The title compound, bp 38–39° (0.1 mm), was prepared in 58% yield from ethyl orthopropionate and ethyl carbamate following the above procedure.

Anal. Calcd for $C_8H_{15}NO_3$: C, 55.52; H, 8.73; N, 8.02. Found: C, 55.43; H, 8.62; N, 8.17.

Registry No.—Tris(carbethoxyamino)methane, 18804-87-0; tris(carbomethoxyamino)methane, 18804-88-1; ethyl *N*-carbethoxyacetimidate, 31084-70-5; ethyl *N*-carbethoxypropioimidate, 31084-71-6.

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Synthesis of Certain Meta Derivatives of *N*-Alkylanilines *via* Aryne Reactions in Primary Aliphatic Amine Solvents[1]

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The sine substitution exhibited by the reaction of ortho-substituted haloaromatic compounds possessing strong $-I$ (electron-attracting by induction) groups [$-OCH_3$, $-Cl$, $-N(CH_3)_2$, $-CN$, etc.] is well established.[2] In addition, we have recently shown that good yields of *N*-alkylanilines can be obtained by allowing benzyne (generated by the action of sodamide on bromobenzene) to react with primary aliphatic amines.[3] It was therefore of interest to determine if comparable yields of meta derivatives of *N*-alkylanilines I could be obtained similarly *via* the corresponding 3-substituted benzyne intermediates.

Since it was anticipated that meta addition would predominate over ortho addition, it was decided to study those substituents which generally are considered to be ortho–para directors. Thus, the reaction of *o*-bromoanisole, *o*-dichlorobenzene, and *o*-chloro-*N*,*N*-dimethylaniline with sodamide in various primary amine solvents was investigated.

Results and Discussion

Table I reports the yields and other pertinent data of the meta-substituted *N*-alkylanilines which were obtained when the corresponding ortho-substituted haloaromatic compounds were treated with sodamide in the presence of various primary alkylamines. From the table it is seen that good to excellent yields of the various *N*-alkylated anilines were obtained. The yields are of the pure meta isomer; the corresponding ortho isomers (2–5%) were readily removed by fractional distillation. Only one of these meta-substituted compounds (*m*-chloro-*N*-isopropylaniline)[4] has been reported, attesting to the excellent synthetic applications of the aryne reaction. Of particular synthetic importance is the convenient syntheses of *N*-alkylanilines containing bulky substituents which are also prone to isomerization, *i.e.*, *sec*-butyl.

Table I
Yields and Physical Data of *N*-Alkyl-Meta-Substituted Anilines, *m*-G-C_6H_4NHR (I)

G	R	Registry no.	Yield,[a] %	Bp, °C (mm)	$n^{25}D$	Analysis, % Calcd	Analysis, % Found
OCH_3	*i*-C_3H_7	31143-05-2	82	110–113 (4)	1.5428	C, 72.69; H, 9.15; N, 8.48	C, 72.55; H, 8.62; N, 8.52
	n-C_3H_7	31084-54-5	85	126–128 (4)	1.5453	C, 72.69; H, 9.15; N, 8.48	C, 73.22; H, 9.12; N, 8.80
	n-C_4H_9	31084-55-6	85	131–134 (4)	1.5372	C, 73.70; H, 9.59; N, 7.82	C, 74.09; H, 9.33; N, 8.16
	i-C_4H_9	31084-56-7	85	115–120 (2)	1.5358	C, 73.70; H, 9.59; N, 7.82	C, 73.94; H, 9.70; N, 7.74
	sec-C_4H_9	31084-57-8	85	108–111 (2)	1.5372	C, 73.70; H, 9.59; N, 7.82	C, 73.66; H, 9.52; N, 7.94
	tert-C_4H_9	31084-58-9	89	103–106 (3)	1.5329	C, 73.70; H, 9.59; N, 7.82	C, 73.62; H, 9.18; N, 7.86
Cl	*i*-C_3H_7	31084-59-0	68	78–80 (0.6)	1.5517	C, 63.72; H, 7.13; N, 8.26	C, 63.66; H, 6.92; N, 8.12
	n-C_3H_7	31084-60-3	79	101–104 (2)	1.5549	C, 63.72; H, 7.13; N, 8.26	C, 63.57; H, 7.16; N, 8.45
	i-C_4H_9	31084-61-4	71	100–103 (1)	1.5531	C, 65.39; H, 7.68; N, 7.63	C, 65.36; H, 7.48; N, 7.55
	sec-C_4H_9	31084-62-5	66	97–99 (1.2)	1.5461	C, 65.39; H, 7.68; N, 7.63	C, 65.39; H, 7.72; N, 7.32
	tert-C_4H_9	19088-39-2	80	80–83 (1)	1.5516	C, 65.39; H, 7.68; N, 7.63	C, 65.39; H, 7.44; N, 7.77
$N(CH_3)_2$	*n*-C_3H_7	31084-64-7	72	115–117 (0.75)	1.5652	C, 74.11; H, 10.18; N, 15.71	C, 73.91; H, 10.26
	i-C_4H_9	31084-65-8	71	117–120 (1)	1.5546	C, 74.95; H, 10.48; N, 14.57	C, 74.74; H, 10.24
	sec-C_4H_9	31084-66-9	67	127–129 (1.1)	1.5558	C, 74.95; H, 10.48; N, 14.57	C, 74.80; H, 10.33
	tert-C_4H_9	31084-67-0	68	110–112 (1.25)	1.5494	C, 74.95; H, 10.48; N, 14.57	C, 74.88; H, 10.48

[a] Yields were obtained using 0.10:0.05 mol ratio of sodium amide to starting material in 100 ml of amine.

Experimental Section

Glpc analyses were performed on a MicroTek instrument Model GC1600 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.—Sodamide was obtained from Fisher Scientific Co., and was used as received. All manipulations of sodamide were carried out in a drybox. 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. *o*-Bromoanisole and *o*-dichlorobenzene, 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.[5]

General Procedure.—All reactions were carried out under a nitrogen atmosphere. To a stirred solution consisting of 100 ml of the appropriate amine solvents and 3.9 g (0.10 mol) of sodamide was added 0.05 mol of the haloaromatic (9.4 g *o*-bromoanisole,

(1) Supported in part by Grant N-118 of the Robert A. Welch Foundation, Houston, Tex.

(2) For a comprehensive listing see R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, pp 136–138.

(3) E. R. Biehl, S. M. Smith, and P. C. Reeves, *J. Org. Chem.*, in press.

(4) C. F. Koelsch and J. W. Britain, *ibid.*, **24**, 1551 (1959).

(5) S. Huenig, *Chem. Ber.*, **85**, 1056 (1952).

7.4 g *o*-dichlorobenzene, or 7.8 g *o*-chloro-*N*,*N*-dimethylaniline). The mixture was then heated to refluxing[6] for 1 hr after the occurrence of a color change (brown except in the case of *o*-bromoanisole, which was deep yellow). At this time the reaction was quenched by the portionwise addition of an excess of ammonium chloride. The amine solvent was then removed by heating with a water bath, and *ca.* 200 ml of ether was added to the residue. After the mixture was stirred for 10 min, it was filtered and the ether solution was extracted with five 50-ml portions of 10% hydrochloric acid.[7] The ether extracts containing the acid-insoluble amines were dried over anhydrous magnesium sulfate. The acid water-soluble layer was then made basic by the addition first of sodium carbonate (until the evolution of carbon dioxide ceased) and then by the addition of a few pellets of sodium hydroxide. This was followed by extraction with three 100-ml portions of ether. After the combined ether extracts were dried ($MgSO_4$) the solvent was removed by a rotary evaporator and the appropriate meta-substituted secondary aromatic amine was obtained by vacuum distillation of the residue.

Glpc analysis revealed that in all cases less than 5% of the undesired ortho isomer was obtained. This isomer, however, was easily removed by one distillation.

(6) The mixture was heated to only 50% in the case of *o*-dichlorobenzene and *sec*- or isobutyl amines.

(7) No acid–base extractions were carried out in the reaction of *o*-chloro-*N*,*N*-dimethylaniline due to the basic mixture of the starting material or in the reaction of *o*-dichlorobenzene in *sec*- or isobutyl amines due to the low basicity of the corresponding *m*-chloro-*N*-alkylanilines.

The Ultraviolet Spectra of Phenolic Aporphines in Basic Solution

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Ultraviolet spectroscopy has proven a valuable tool for the structural elucidation of aporphine alkaloids. For instance, 1,2,9,10-tetrasubstituted aporphines show absorption maxima in 95% ethanol near 220, 282, and 305 mμ, while in the 1,2,10,11 series the maxima lie near 220, 270, and 305 mμ.[1-4]

In the present study, the uv spectra of a variety of monophenolic aporphines were measured in ethanol solution with a little aqueous NaOH added.[5] The presence of a phenolic function at C-9 results in a bathochromic shift which is also accompanied by a strong hyperchromic effect between 315 and 330 mμ and a minimum between 269 and 274 mμ. This is true whether the aporphine is trisubstituted as in anolobine (Figure 1) or tetrasubstituted as in actinodaphnine and *N*-methyllaurotetanine or even pentasubstituted as in cassyfiline (Figure 2). For comparison purposes, the uv spectral values in 95% ethanol for anolobine, actinodaphnine, *N*-methyllaurotetanine hydrobromide, and cassyfiline are listed in Table I.

Monophenolic aporphines such as corydine, isothebaine, *N*-methyl-10-methylhernovine (1,10,11-trime-

(1) M. Shamma, *Experientia*, **16**, 484 (1960).
(2) M. Shamma and W. A. Slusarchyk, *Chem. Rev.*, **64**, 59 (1964).
(3) M. Shamma in "The Alkaloids," Vol. IX, R. H. F. Manske, Ed., Academic Press, New York, N. Y., 1967, p 1.
(4) A. W. Sangster and K. L. Stuart, *Chem. Rev.*, **65**, 69 (1965).
(5) Each spectrum was first recorded in 95% ethanol using a 1-cm standard quartz cell. The alkaloid concentration was about 16 mg/l. Two drops of aqueous 1 *N* NaOH solution were then added to the cell solution and the spectrum was rerun.

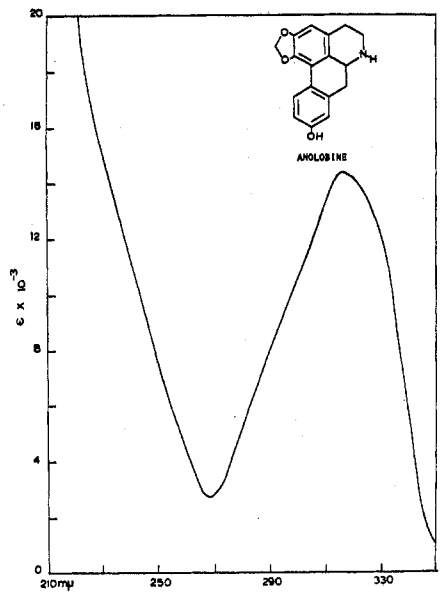

Figure 1.—Uv spectrum of anolobine in basic solution.

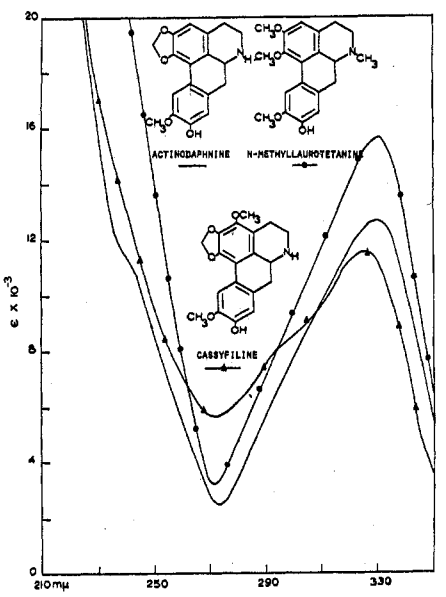

Figure 2.—Uv spectra of actinodaphnine, *N*-methyllaurotetanine, and cassyfiline in basic solution.

TABLE I
UV SPECTRA OF SOME APORPHINES IN 95% ETHANOL

Anolobine	λ_{max} 215, 238 sh, 280, 292 sh, and 320 mμ sh (log ε 4.21, 3.87, 4.05, 3.99, and 3.33)
Actinodaphnine	λ_{max} 219, 232 sh, 273 sh, 282, 306, and 313 mμ sh (log ε 4.17, 4.09, 3.77, 3.87, 3.92, and 3.90)
N-Methyllaurotetanine HBr	λ_{max} 219, 271 sh, 282, 303, and 313 mμ sh (log ε 4.49, 3.96, 4.06, 4.09, and 4.04)
Cassyfiline	λ_{max} 219, 240 sh, 273 sh, 283, 303, and 315 mμ sh (log ε 4.11, 3.92, 3.73, 3.84, 3.81, and 3.78)