1-Chlorobenzo[*g*]phthalazine was isolated as tan crystals, 0.7 g (16% overall), mp 178–180°.

Anal. Calcd for $C_{12}H_7N_2Cl$: N, 13.05; Cl, 16.52. Found: N, 12.84; Cl, 16.18.

1-Chloro-4-methoxybenzo[*g*]phthalazine (XI).—A solution of sodium (0.23 g, 001 g-atom) in methanol (150 ml) was treated with IX (2.49 g, 0.01 mol). The mixture was refluxed under nitrogen for 2 hr and then concentrated to dryness *in vacuo*. The residue was extracted with boiling methylene chloride (100 ml), evaporated to dryness *in vacuo*, and recrystallized from benzene to yield XI as tan crystals, 1.66 g (68%), mp 134–136°.

Anal. Calcd for $C_{13}H_9N_2OCl$: N, 11.44; Cl, 14.49. Found: N, 11.37; Cl, 14.19.

Kinetics.—The procedure, using a divided flask, was essentially as previously described except that the flask was closed with a septum through which aliquots for estimation were removed by calibrated syringe.[2] For runs at 70° a standard sealed ampoule method was employed. To measure the reaction rates for IX at 0°, V, X, and XI at 25°, III at 55°, and VI at 70°, aliquots for estimation were partitioned between a known volume of 0.1 *M* perchloric acid and methylene chloride. The chloride ion concentration in the aqueous phase was determined using a specific ion electrode (Orion Model 92-17) and a Beckman Expandomatic pH meter, and calibration curves were prepared from standard chloride ion solutions. As before, runs were made in triplicate and the concentrations varied by a factor of 4 with respect to each other except for those compounds run under pseudo-first-order conditions.

Calculations.—The rate constants were obtained from a least-squares analysis of the relevant expressions: $\ln a/(a - x)$ or $[1/(b - a)] \ln [a(b - x)/b(a - x)]$ *vs.* time. Calculations were carried out on an IBM 1130 computer. ΔH^* and ΔS^* were determined as described by Bunnett.[23]

Product Analysis.—The products of the reaction of I, II, IV, and VI were obtained from reactions of 0.01 mol of these phthalazines with an equimolar amount of sodium methoxide in methanol. The solvent was evaporated and the residue extracted with boiling methylene chloride. Evaporation and recrystallization from benzene yielded the products: from I, 1-chloro-4-methoxyphthalazine (66%), mp 107–108° (lit.[20] mp 107–108°); from II, 1-methoxyphthalazine (82%), mp 61–62° (lit.[17] mp 60–61°); from IV, 1-methoxy-4-methylphthalazine (71%), mp 71–72° (lit.[24] mp 53–54°), and 1,4-dimethoxyphthalazine (81%), mp 93° (lit.[15] mp 93°).

Registry No.—I, 4752-10-7; II, 5784-45-2; III, 10132-01-5; IV, 19064-68-7; V, 2258-89-1; VI, 19064-71-2; VII, 13580-86-4; VIII, 2257-69-4; IX, 30800-67-0; X, 30800-68-1; XI, 30800-69-2.

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(23) J. F. Bunnett, *Tech. Org. Chem.*, **8**, 199 (1961).

(24) F. M. Rowe and A. T. Peters, *J. Chem. Soc.*, 1331 (1933). The nmr spectrum was consistent with the structure: δ 2.36 (s, 3 H, CH_3), 3.84 ppm (s, 3 H, OCH_3).

Synthesis of Tris(carboalkoxyamino)methane and *N*-Carbethoxyiminocarboxylic Acid Esters[1]

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Only a few tris(amino)methane derivatives of the general structure $HC(NHR)_3$ are known. Tris(formamido)methane (*N*,*N'*,*N''*-methylidynetrisformamide) and tris(acetamido)methane were reported by Pinner[2] in 1883. Several higher homologs of this series were recently synthesized by Bredereck, *et al.*,[3] by heating ethyl orthoformate with amides in the presence of a catalytic amount of sulfuric acid.

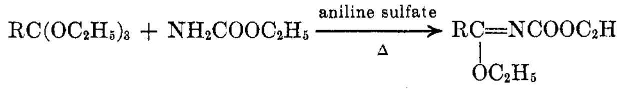
We have now synthesized tris(carboalkoxyamino)-methanes by heating ethyl orthoformate with alkyl carbamates and using aniline sulfate as the catalyst.

$$HC(OC_2H_5)_3 + NH_2COOR \xrightarrow[\Delta]{\text{aniline sulfate}} HC(NHCOOR)_3 + C_2H_5OH$$

$$R = CH_3, C_2H_5$$

The compounds, obtained in 45–55% yields, were characterized by elemental analysis and nmr spectra. The proton nmr spectrum of tris(acetamido)methane (see Experimental Section) is similar to that of tris(carbethoxyamino)methane.

Reactions of higher ortho esters with urethane under similar reaction conditions were found to give different products. Thus, urethane reacted with triethyl orthoacetate or triethyl orthopropionate to give ethyl *N*-carbethoxyacetimidate and ethyl *N*-carbethoxypropioimidate, respectively. *N*-Carbethoxyiminocarboxylic acid esters are colorless liquids, sparingly soluble in water, and stable at room temperature.



$$RC(OC_2H_5)_3 + NH_2COOC_2H_5 \xrightarrow[\Delta]{\text{aniline sulfate}} RC(OC_2H_5){=}NCOOC_2H_5$$

$$R = CH_3, C_2H_5$$

Experimental Section

Tris(carbethoxyamino)methane.—A mixture containing 40 g (0.27 mol) of ethyl orthoformate, 74 g (0.81 mol) of ethyl carbamate, and 0.7 g of aniline sulfate was heated in a distillation apparatus at 115–125° for 2.5 hr. During this time 32 ml of ethanol distilled over. The temperature was then increased to 155° for 1.5 hr, and an additional 13 ml of ethanol was removed. The reaction mixture was cooled and the crude material was recrystallized from methylene chloride to give 41 g (55% yield) of tris(carbethoxyamino)methane, a white, crystalline solid, mp 210–211°.

Anal. Calcd for $C_{10}H_{19}N_3O_6$: C, 43.31; H, 6.91; N, 15.16. Found: C, 43.11; H, 6.82; N, 15.03.

Proton nmr (DMSO-d_6) showed δ 7.45 (d, J = 7.0 Hz, 3, NH), 6.24 (q, J = 7.0 Hz, 1, CH), 4.03 (q, J = 7.1 Hz, 6, CH_2), and 1.20 (t, J = 7.0 Hz, 9, CH_3).

The proton nmr spectrum (DMSO) of tris(acetamido)methane showed δ 7.42 (d, J = 7.2 Hz, 3, NH), 6.12 (q, J = 7.0 Hz, 1, CH), and 3.62 (s, 9, CH_3).

Tris(carbomethoxyamino)methane.—The title compound was synthesized from ethyl orthoformate and methyl carbamate in 45% yield following the above procedure. The crude solid was crystallized from methanol, mp 177–178°.

Anal. Calcd for $C_7H_{13}N_3O_6$: C, 35.74; H, 5.57; N, 17.87. Found: C, 36.11; H, 5.62; N, 17.81.

In a separate experiment, a mixture of ethyl orthoformate and methyl carbamate was heated at 145° for 2 hr in the absence of aniline sulfate. No ethanol was liberated and only the starting materials were isolated from the reaction mixture at the end of the experiment.

Ethyl *N*-Carbethoxyacetimidate.—A mixture containing 32.5 g (0.2 mol) of ethyl orthoacetate, 60 g (0.4 mol) of ethyl carbamate, and 0.7 g of aniline sulfate was heated in a distillation apparatus at 110–120° for 1.5 hr. During this time 20 ml of ethanol was distilled. The reaction mixture was cooled to 5° and the excess of ethyl carbamate was removed by filtration. The filtrate was dissolved in 150 ml of carbon tetrachloride and the solution was washed with four 100-ml portions of water in order to remove the remaining ethyl carbamate. The carbon tetrachloride solution was distilled to give 21 g (66% yield) of a colorless liquid, bp 90–91° (25 mm).

Anal. Calcd for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80. Found: C, 52.51; H, 8.61; N, 8.97.

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[1] This work was supported by the Office of Naval Research. The experimental work was performed at the Aerojet-General Corp., Azusa, Calif.

[2] A. Pinner, *Ber.*, **16**, 357, 1647, 1660 (1883); **17**, 172 (1884).

[3] H. Bredereck, F. Effenberger, and H. J. Treiber, *ibid.*, **96**, 1505 (1963).

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]

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	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.

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.

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,

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[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).