

Condensation of Chloroacetophenone with Ethanol- and Diethanol-amine and of Chloroacetocatechol with β -Methoxyethylamine¹

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Chloroacetophenone reacts readily with ethanol-amine. The product, $\text{PhCOCH}_2\text{NHCH}_2\text{CH}_2\text{OH}$, melts at 144° . *Anal.* N calcd., 7.82; found, 7.79. Diethanolamine is less reactive; long boiling in benzene solution is required to form $\text{PhCOCH}_2\text{-N}(\text{CH}_2\text{CH}_2\text{OH})_2$. The hydrochloride was precipitated from the washed and dried benzene solution by hydrogen chloride. The base was set free by concd. sodium hydroxide solution and taken up in ether. Recrystallized from alcohol it melted at 44° . *Anal.* N calcd., 6.27; found, 6.25.

Chloroacetocatechol reacts readily with β -methoxyethylamine. The base, $(\text{HO})_2\text{C}_6\text{H}_3\text{-COCH}_2\text{NHCH}_2\text{CH}_2\text{OCH}_3$, melts at 93° . *Anal.* N calcd., 6.22; found, 6.17. The hydrochloride melts at 186° . *Anal.* Cl calcd., 13.56; found, 13.49.

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Aryl Diazomorpholides

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In the course of some work with morpholine the aryl diazomorpholides listed in the accompanying table were prepared by convenient methods² from morpholine and aqueous solutions of diazotized arylamines. They are readily purified.

These compounds are remarkably stable in the solid state. Their behavior with the common mineral acids is similar to that of the aryl diazopiperidides.^{2b} In the presence of molecular quantities of acetic acid they condense with benzene to diphenyl derivatives³; better yields are obtained if anhydrous aluminum chloride is employed as the condensing agent.⁴ Hot acetic anhydride is without effect.

With iodic acid the azo linkage is oxidized in part to the nitro group. Thus, when 2.7 g. of *p*-bromobenzenediazo-

(1) Present address: Procter and Gamble Co., Cincinnati, Ohio.
(2a) Baeyer and Jaeger, *Ber.*, **8**, 148, 893 (1875); (b) Wallach, *Ann.*, **235**, 233 (1886); (c) Noelting and Binder, *Ber.*, **20**, 3004 (1887).

(3) Compare with Kühling, *Ber.*, **28**, 41 (1895); Bamberger, *ibid.*, **28**, 403 (1895); Gerngross and Dunkel, *ibid.*, **57**, 742 (1942).

(4) Möhlau and Berger, *ibid.*, **26**, 1196, 1994 (1893).

TABLE I

R	M. p., ^a °C.	Color	Nitrogen, % ^b	
			Calcd.	Found
Phenyl	29-30	White	21.98	22.07
2-Methylphenyl	32-33	Tan	20.48	20.29
4-Methylphenyl	49.5-50.5	White	20.48	20.52
α -Naphthyl	82-83	Brown-orange	17.42	17.52
β -Naphthyl	99.5-100.5	Orange	17.42	17.50
2,6-Dimethylphenyl	Oil	Yellow	19.17	19.24
4-Diphenyl	110.5-111	White	15.72	15.73
4,4'-Diphenyl	253-255	Yellow	22.10	22.07
3,3'-Dimethyl-4,4'-diphenyl	140.5-141.5	Gold	20.58	20.38
3-Nitrophenyl	83-84	Yellow	23.72	23.80
4-Nitrophenyl	137.5-138.5	Yellow	23.72	23.67
2-Chlorophenyl	20-22	White	18.62	18.71
3-Chlorophenyl	Oil	Orange	18.62	18.61
4-Chlorophenyl	54-55	White	18.62	18.58
2,5-Dichlorophenyl	76-77	White	16.16	16.08
3-Bromophenyl	33-34	White	15.56	15.72
4-Bromophenyl	89.5-90	White	15.56	15.61
4-Iodophenyl	140.5-141.5	White	13.25	13.01
4-Chloro-2-methylphenyl	59-60	White	17.53	17.53
3-Bromo-4-methylphenyl	48.5-49.5	White	14.79	14.87
3,5-Dibromo-4-methylphenyl	87-88	White	11.58	11.62
4-Methoxyphenyl	69-70	White ^c	19.00	18.88
4-(4-Morpholinyl)-phenyl ^d	209-211	Gold	20.28	20.05

^a M. p.'s corrected. ^b Micro-Dumas. ^c Darkens rapidly in air. ^d With concd. hydrobromic acid the new compound 4-(*p*-bromophenyl)-morpholine is formed: rhombic plates from dilute alcohol; m. p. $114.5-115.5^\circ$. *Anal.* Calcd. for $\text{C}_{10}\text{H}_{12}\text{ONBr}$: N, 5.79. Found: N, 5.86. The hydrochloride decomposes $192-194^\circ$.

morpholide and 3.6 g. of iodic acid in 5 cc. of water were refluxed for one-half hour, purple vapors of iodine were given off. The product obtained on steam distillation (0.2 g.), when recrystallized from 95% alcohol, melted at 90° (7% yield), and showed no depression of the melting point when mixed with *p*-iodobromobenzene. The black tar remaining in the distilling flask was extracted twice with boiling water and once with a small amount of hot alcohol. The residue was taken up in benzene, decolorized, and the needles obtained on evaporation recrystallized twice from alcohol; m. p. 169° ; mixed m. p. with *p*-iodonitrobenzene, 169° .

Sulfur dioxide reacts with these compounds to give stable intermediate products whose structure has not yet been determined. Thus, 1 g. of the diazo compound in 20 g. of acetone-alcohol (50-50), cooled to zero degrees, was saturated with sulfur dioxide, allowed to stand one hour, heated to boiling, and poured into 25 cc. of water. The precipitate was filtered and recrystallized from water or alcohol. They are all difficultly soluble in cold, but readily soluble in hot water. The following individual products were obtained: from benzenediazomorpholide, 0.8 g., m. p. $142-143.5^\circ$, N 10.93%; with *p*-bromobenzenediazomorpholide, yield of silky needles from alcohol, 0.9 g., m. p. $155-156^\circ$, N, 7.71, 7.72%; with β -naphthalenediazomorpholide, 0.3 g., m. p. $181-182.5^\circ$, N, 8.98%. These products were not soluble in, or decomposed by heating with, concentrated hydrochloric acid; they dissolved in cold alkali solution, and then slowly decomposed. One gram of the product