Condensation of Chloroacetophenone with Ethanol- and Diethanol-amine and of Chloroacetocatechol with β-Methoxyethylamine[1]

BY K. W. BRIGHTON AND E. EMMET REID

Chloroacetophenone reacts readily with ethanolamine. The product, $PhCOCH_2NHCH_2CH_2OH$, melts at 144°. *Anal.* N calcd., 7.82; found, 7.79. Diethanolamine is less reactive; long boiling in benzene solution is required to form $PhCOCH_2N(CH_2CH_2OH)_2$. 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, $(HO)_2C_6H_3COCH_2NHCH_2CH_2OCH_3$, 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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[1] From a part of the Dissertation of K. W. Brighton, June, 1936 Original manuscript received March 23, 1942.

CONTRIBUTION FROM THE
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Aryl Diazomorpholides

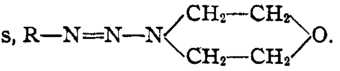
BY RONALD A. HENRY[1] AND WILLIAM M. DEHN

In the course of some work with morpholine the aryl diazomorpholides listed in the accompanying table were prepared by convenient methods[2] 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 derivatives[3]; better yields are obtained if anhydrous aluminum chloride is employed as the condensing agent.[4] Hot acetic anhydride is without effect.

TABLE I

ARYL DIAZOMORPHOLIDES,



$R{-}N{=}N{-}N\left\langle\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH_2\end{matrix}\right\rangle O.$

R	M. p.,[a] °C.	Color	Nitrogen, %[b] Calcd.	Nitrogen, %[b] 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°. *Anal.* Calcd. for $C_{10}H_{12}ONBr$: N, 5.79. Found: N, 5.86. The hydrochloride decomposes 192–194°.

With iodic acid the azo linkage is oxidized in part to the nitro group. Thus, when 2.7 g. of *p*-bromobenzenediazomorpholide 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°, N 10.93%; with *p*-bromobenzenediazomorpholide, yield of silky needles from alcohol, 0.9 g., m. p. 155–156°, N, 7.71, 7.72%; with β-naphthalenediazomorpholide, 0.3 g., m. p. 181–182.5°, 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

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[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).

from *p*-bromobenzenediazomorpholide was refluxed for ten minutes with 1 g. of sodium hydroxide in 10 cc. of water. Ten cc. more of water was added and the solution filtered from a small amount of tar. On making the filtrate acid with concentrated hydrochloric acid, cream-colored needles separated. These needles dissolved in hot concentrated sulfuric acid to give a blue color; a mixed m. p. with a sample of *p*-bromobenzenesulfinic acid showed no depression.

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The Preparation of Cholesteryl *p*-Aminobenzoate

BY DAVID KRITCHEVSKY

In the preparation of cholesteryl *p*-aminobenzoate by reduction of cholesteryl *p*-nitrobenzoate, Shriner and Ko[1] were unable to effect reduction using iron, tin and amalgamated zinc with hydrochloric acid and finally reduced the nitro compound catalytically.

The reduction by chemical means was re-investigated and a suitable procedure using iron powder and acetic acid was found.

Experimental Part

Cholesteryl *p*-Nitrobenzoate.—The esterification was carried out by the method of Einhorn and Hollandt.[2] Cholesterol (25 g.) and *p*-nitrobenzoyl chloride (14.5 g.) (purified by vacuum distillation) were weighed into a 400-cc. beaker and 50 cc. of pyridine was added. The mixture was slowly heated to boiling; the acid chloride and the cholesterol dissolving during the heating. The solution was allowed to boil for one minute and then allowed to cool. A light brown solid began to crystallize instantly. Two recrystallizations from boiling methyl cellosolve gave large, white almost transparent plates, 25.7 g. (74% based on cholesterol used). The purest compound obtained melted at 190.5–191.5° and possessed a specific rotation in chloroform, $[\alpha]^{20}_{\mathrm{D}}$ −6.97°.

Cholesteryl *p*-Aminobenzoate.—Cholesteryl *p*-nitrobenzoate (6 g.) was placed in a 200-cc. round-bottomed flask with 80 cc. of glacial acetic acid, 3.5 g. of 100 mesh iron filings was added and the mixture allowed to boil under gentle reflux. The color of the solution changed from colorless to dark brown within the first half hour. After one and one-half hours all the *p*-nitrobenzoate had dissolved. The solution was allowed to boil under reflux for one hour longer. The solution was then poured into a beaker and allowed to cool, crystals separating instantly. The crystals were washed with 1 *N* hydrochloric acid until the washings were colorless and then with water until the washings were neutral to litmus. The crude product weighed 5 g. Two recrystallizations from boiling amyl acetate yielded large tan needles, 4.2 g. (76% calculated). The purest compound obtained melted at 237.8–238.8° and possessed a specific rotation in chloroform, $[\alpha]^{20}_{\mathrm{D}}$ +3.68°.

Saponification.—For the saponification of the cholesteryl *p*-aminobenzoate 0.1508 g. of the compound was boiled under reflux with 16 cc. of 0.9864 *N* alcoholic sodium hydroxide for two and one-half hours. A titer of 30.95 cc. of 0.5000 *N* hydrochloric acid was required to neutralize the excess alkali. Saponification equivalent found, 503: calculated, 505. The cholesterol recovered weighed 0.1036 g. (90% recovery based on *p*-aminobenzoate used) and melted at 147–148°. The melting point of the cholesterol used in these experiments was 145–146°. The *p*-aminobenzoic acid recovered from the saponification melted at 183° and did not depress the melting point of a known sample of *p*-aminobenzoic acid.

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RECEIVED NOVEMBER 30, 1942

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[1] Shriner and Ko, *J. Biol. Chem.*, **80**, 1 (1928).

[2] Einhorn and Hollandt, *Ann.*, **301**, 95 (1898).

Hydrate Isomerism in the Hydrated Chromic Chlorides. Preparation of Triethylenediamine Chromium(III) Chloride from Hexaquo Chromium(III) Chloride[1]

BY LOUIS E. MARCHI[2] AND JAMES P. MCREYNOLDS

Triethylenediamine chromium(III) chloride, $[\mathrm{Cr(en)_3}]\mathrm{Cl_3}$,[3] may be prepared from the violet hexaquo-chromium(III) chloride by reaction with anhydrous ethylenediamine.

Procedure

Triethylenediamine Chromium(III) Chloride.—The violet hexaquo-chromium(III) chloride was prepared by the method of Biltz and Biltz.[4] Forty grams of the violet chloride was added to 100 ml. of anhydrous toluene in a 3-necked, 500 ml., round-bottomed flask equipped with a stirrer, thermometer and separatory funnel. The flask and its contents were cooled to 0° and anhydrous ethylenediamine[5] added slowly at first. The temperature was never allowed to rise above 15°. During the course of the reaction the mixture became red colored, due to the formation of some red dichlorodiethylenediamine chromium(III) chloride monohydrate, $[\mathrm{Cr\ en_2Cl_2}]\mathrm{Cl\cdot H_2O}$, which masked the yellow color of the $[\mathrm{Cr\ en_3}]\mathrm{Cl_3}$. The mixture was stirred for one-half hour after the addition of the ethylenediamine, after which time the toluene layer was poured off. The thick red aqueous solution was diluted to twice its volume and treated with "Super-cel."

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[1] Abstracted from a thesis presented to the Faculty of the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in August, 1942.

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[3] en = enthylenediamine, $\mathrm{NH_2{-}CH_2{-}CH_2{-}NH_2}$.

[4] Biltz and Biltz (trans. by Hall and Blanchard), "Laboratory Methods of Inorganic Chemistry," 1928, p. 200.

[5] The ethylenediamine was prepared by the method of Putnam and Kobe, *Trans. Electrochem. Soc.*, **74**, 610 (1938). The round-bottomed flask recommended was replaced by an iron container, the use of which circumvented the etching encountered by the contact of hot concentrated solutions of sodium hydroxide with glass.