[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Condensations of Aromatic Amines with Formaldehyde in Media Containing Acid. VII. The Polymeric States and Structures of Some Anhydro-*p*-(alkylamino)-benzyl Alcohols

BY W. S. YOUNG AND E. C. WAGNER

Anhydro-*p*-alkylaminobenzyl alcohols of the type $\left[{}^{R}\!\!>NC_6H_4CH_2—\right]_n$, or their salts, have been reported from six alkylarylamines, *viz.*, methyl-, ethyl-, *n*-propyl-, *n*-butyl-, isoamyl- and benzyl anilines.[1–4] Only the methyl, ethyl and benzyl compounds have hitherto been isolated as bases,[2,4] and of these only the first has been well characterized. Friedländer[4] found for the methyl compound a molecular weight of 224, and reported it to be dimeric. He established its essential structure by reduction to methyl-*p*-toluidine. In like manner the salts of other bases of this type were shown[3] to have the same structure.

Knowledge of the anhydro-*p*-alkylaminobenzyl alcohols is so meager that a more careful characterization of the compounds mentioned was undertaken. The six bases were isolated in a state of purity from the purified hydrochlorides. Their essential structural identity was shown by reduction to the corresponding alkyl-*p*-toluidines. Molecular weight determinations in benzene, with precautions to minimize error due to moisture absorbed from the atmosphere, failed to confirm Friedländer's value for anhydro-*p*-methylaminobenzyl alcohol. This base, and all the others, were found to be trimeric, *viz.*, $\left[{}^{R}\!\!>NC_6H_4CH_2—\right]_3$. A cyclic structure is probable and would be strain-free.[5] Molecular weights determined in molten camphor were much higher, indicating further polymerization by heat. The bases, and to a less degree the hydrochlorides, are not very stable and on keeping acquire a yellow to orange color. Table I presents molecular weights, melting points and analytical values for the six bases. Results of the reduction experiments are mentioned in the experimental part.

The six bases were made also by the use of methylal instead of formaldehyde. A temperature of about 50° was necessary to disengage formaldehyde in the reaction mixtures, and as this temperature was favorable also to the formation of diphenylmethane bases[6] the method appeared to be without advantage.

Experimental

General.—The alkylanilines used were redistilled Eastman Kodak Company products; benzylaniline was a Kahlbaum specimen.

Boiling points of alkyl-*p*-toluidines obtained in the reduction experiments were determined by Siwoloboff's method.

Molecular weights in benzene were determined with a P. T. R. Beckmann thermometer in the presence of anhydrous barium perchlorate, as recommended by Rall and Smith,[7] and with an air-sealed mechanical stirrer to minimize interference by atmospheric moisture. The cryoscopic constant of the benzene was determined using pure naphthalene. Molecular weights in camphor were determined by the procedure of Rast, using a turpentine thermometer.

Preparation of Hydrochlorides of Anhydro-*p*-alkylaminobenzyl Alcohols.—The method described previously[3] was employed with slight changes as required in individual cases. Salts of the methyl-, ethyl-, *n*-propyl- and *n*-butyl compounds were made in water solution. To obtain the hydrochlorides of the isoamyl and benzyl bases it was found better to dissolve the alkylaniline in several parts of U. S. P. alcohol, add a slight excess of concd. hydrochloric acid, dilute with water and then add to the chilled mixture the required formalin. Benzylaniline separated at first as its hydrochloride, which dissolved progressively as the anhydro-*p*-benzylaminobenzyl alcohol hydrochloride formed and crystallized out.

The filtered anhydro-*p*-alkylaminobenzyl alcohol hydrochlorides were washed thoroughly with alcohol and then ether. This operation was found to be important, especially with the *n*-butyl and isoamyl compounds, whose salts were slimy as first obtained. The alcohol and ether removed resinous or oily impurities which otherwise later contaminated the isolated bases and impeded their crystallization. The salts so obtained were pure white, and unlike specimens prepared without effective washing,[3] approached analytical purity.

Preparation of the Anhydro-*p*-alkylaminobenzyl Alcohol Bases.—The washed and dried salt was suspended in about five parts of alcohol chilled in ice. The mixture was stirred mechanically and 20% aqueous sodium hydroxide solution was added slowly to alkalinity. Stirring and chilling were

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[1] Goldschmidt, *Chem.-Ztg.*, **24**, 284 (1900); **26**, 606, 967 (1902).

[2] German Patent 97,710, *Friedl.*, **5**, 94 (1901).

[3] Wagner, THIS JOURNAL, **55**, 724 (1933).

[4] Friedländer, *Monatsh.*, **23**, 973 (1902).

[5] Private communication from Dr. E. H. Cox, of Swarthmore College. Construction of the cyclic trimer, using precision atomic models, showed the molecule to be entirely strain-free.

[6] Von Braun, *Ber.*, **41**, 2145 (1908); Rivier and Farine, *Helv. Chim. Acta*, **12**, 865 (1929); Wagner, THIS JOURNAL, **56**, 1944 (1934).

[7] Rall and Smith, *Ind. Eng. Chem., Anal. Ed.*, **8**, 324 (1936).

TABLE I

SOME ANHYDRO-*p*-ALKYLAMINOBENZYL ALCOHOLS

Compound $\mathrm{R}{>}NC_6H_4CH_2$— R	M. p. (corr.) °C.	Molecular weights In benzene found[a]	Calcd. trimer	In camphor	Analyses Carbon,[f] % Calcd.	Found	Hydrogen,[f] % Calcd.	Found	Nitrogen, % Calcd.	Found
Methyl	209–12[b]	351[c]	357	2070					11.8	11.4[g]
Ethyl	84–6[d]	396	399	1500					10.5	10.4[g]
n-Propyl	106–8	447	441	1350	81.6	81.6	8.84	8.83	9.5	9.35[g]
n-Butyl	52–3	484	483	1670	82.0	81.8	9.32	9.25	8.7	8.7[h]
i-Amyl	46–8	508	525	1470	82.3	82.2	9.71	9.73	8.0	8.3[h]
Benzyl	162–3[e]	579	585	1570	86.2	86.1	6.67	6.56	7.2	7.1[g]

[a] Averages of from two to five values. [b] Previously reported[2,3]: 210°, 205–210°. [c] Friedländer[4] found 224. [d] Previously reported[2,4]: 86°, 79–80°. [e] Previously reported[2]: 161°. [f] Semi-micro method. Analyses by Wm. McClellan. [g] Semi-micro Kjeldahl method. Analyses by F. W. Landau. [h] Micro Dumas method. Analyses by Edw. D'Ouville.

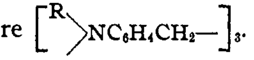
continued some minutes longer, and any lumps of base were broken up. The mixture was treated with several volumes of ice water, and the precipitated base was filtered off and washed with cold 50% alcohol. It was dried in a vacuum desiccator and then crystallized. The methyl compound was satisfactorily crystallizable from benzene, and the other compounds from ligroin (70–90°). The *n*-butyl and isoamyl compounds were very soluble in ligroin, and their recovery necessitated evaporation of part of the solvent; the isoamyl compound required considerable manipulation to induce crystallization.

The bases were crystalline and white, but became discolored on standing. Melting points were not in all cases sharp; it is possible that melting was accompanied by incipient decomposition or by change in polymeric state. The melting points of homologous bases showed "alternation."

Reduction of Anhydro-*p*-alkylaminobenzyl Alcohols to Alkyl-*p*-toluidines.—Reduction was effected using zinc dust and hot dilute sulfuric acid as previously described.[3] The alkyl-*p*-toluidines from new bases were identified by their boiling points and by melting points of their hydrochlorides. The values obtained were as follows: (1) *n*-propyl-*p*-toluidine, b. p. 237–240°; hydrochloride, m. p. 154–155°, (2) *n*-butyl-*p*-toluidine, b. p. 251–252°; hydrochloride, m. p. 148–149°, (3) isoamyl-*p*-toluidine, b. p. 266–267°; hydrochloride, m. p. 139–142°, (4) benzyl-*p*-toluidine, b. p. 318–320°; hydrochloride, m. p. 180–181°. The hydrochlorides of *n*-butyl- and isoamyl-*p*-toluidines were identified also by mixed melting point tests.

Summary

1. Three new bases of the anhydro-*p*-alkylaminobenzyl alcohol series have been prepared, and together with three bases previously known, have been characterized with respect to polymeric state and structure.

2. The six bases were found to be trimeric in benzene solution, a finding at variance with Friedländer's conclusion that anhydro-*p*-methylaminobenzyl alcohol is dimeric. In molten camphor polymerization was found to be extensive. Strong reduction split the bases into the corresponding alkyl-*p*-toluidines, showing them to have the structure  $\left[\mathrm{R}{>}NC_6H_4CH_2\text{—}\right]_3$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Alkenyl Esters Derived from Alkylacetylenes[1]

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Introduction

It was reported in a previous paper[2] that addition of bromine to the 2-acyloxy-1-alkenes derived from alkylacetylenes was followed by spontaneous cleavage yielding an acyl bromide and a monobromomethyl alkyl ketone. Further study has revealed that a number of other agents effect similar cleavage.

As in the case of bromination these esters react readily with hydrogen bromide and chloride. The addition compounds are unstable and cleave to yield the acyl halide and corresponding methyl alkyl ketone. The reactions may be represented as

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[1] Paper XX on the chemistry of the alkylacetylenes and their addition compounds; previous paper, *J. Org. Chem.*, **1**, in press (1937).

[2] Slanina, Hennion and Nieuwland, THIS JOURNAL, **58**, 891 (1936).