

TABLE I
AMIDES AND HETEROCYCLIC COMPOUNDS FROM PHENYL SALICYLATE AND FROM PHENYL-1-HYDROXYNAPHTHALENE-2-CARBOXYLATE

Amine used	M. p., °C.	Yield, %	Formula	% Nitrogen	
				Calcd.	Found
With Phenyl Salicylate					
Piperidine	142-143	69	C ₁₂ H ₁₅ NO ₂	6.8	6.9
Cyclohexylamine	85-86	79	C ₁₃ H ₁₇ NO ₂	6.4	6.4
Benzylamine	135-136	77	C ₁₄ H ₁₃ NO ₂	6.2	6.2
<i>n</i> -Butylamine ¹¹	^a	81			
Laurylamine	71-72	75	C ₁₉ H ₃₁ NO ₂	4.6	4.6
Diethylamine	^b	68	C ₁₁ H ₁₅ NO ₂	7.3	7.2
Ethylenediamine	183-184	69	C ₁₀ H ₁₆ N ₂ O ₄	9.4	9.5
Chloroaniline	155	83	C ₁₃ H ₁₁ ClNO	15.3 ^c	15.0 ^c
Aminobiphenyl	110	85	C ₁₉ H ₁₅ NO ₂	^d	^d
<i>o</i> -Aminophenol	125	22.4	C ₁₃ H ₉ NO ₂	6.63 ^e	6.63 ^e
<i>p</i> -Aminophenol ¹²	176	57			
<i>m</i> -Aminophenol	184	58	C ₁₃ H ₁₁ NO ₂	6.11	6.10
5-Aminoindazole	239	37	C ₁₄ H ₁₁ N ₃ O ₂	16.62	16.57
6-Aminoindazole	234-235	31	C ₁₄ H ₁₁ N ₃ O ₂	16.62	16.56
<i>m</i> -Phenylenediamine ¹²	199-200	49			
5-Aminobenzotriazole	245	42	C ₁₃ H ₁₀ N ₄ O ₂	22.03	21.74
1,2,3,4-Tetrahydroquinoline	138-139	34	C ₁₆ H ₁₆ NO ₂	5.5	5.6
With Phenyl-1-hydroxynaphthalene-2-carboxylate					
Diethylamine	^f	63	C ₁₅ H ₁₇ NO ₂	5.77	5.6
<i>o</i> -Phenylenediamine	> 265	78	C ₁₇ H ₁₂ N ₂ O	^g	^g
<i>o</i> -Aminophenol	188	89	C ₁₇ H ₁₁ NO ₂	^h	^h

^a B. p. 153-156° (3 mm.). ^b B. p. 146-148° (4 mm.). ^c Chlorine. ^d Calcd.: C, 78.80; H, 5.18. Found: C, 78.8; H, 5.1. ^e Calcd.: C, 73.8; H, 4.3. Found: C, 74.24; H, 4.53. ^f B. p. 130-133° (1 mm.). ^g Calcd.: C, 78.40; H, 4.6. Found: C, 78.6; H, 4.4. ^h Calcd.: C, 78.0; H, 4.22. Found: C, 77.9; H, 4.3.

acetanilide⁹ or aniline¹⁰, from methyl salicylate and an aliphatic amine.^{11,12}

(9) German Patent 289,027 [*Frdl.*, **12**, 184 (1914-1916)].

(10) Schöpf, *Ber.*, **25**, 2740 (1892).

(11) Hurd, Fancher and Bonner, *THIS JOURNAL*, **68**, 2745 (1946).

(12) Fargher, Galloway and Probert, *J. Textile Inst.*, **21**, 245T (1930) [*C. A.*, **24**, 6026 (1930)].

COMMUNICATION No. 1154

KODAK RESEARCH LABORATORIES

ROCHESTER 4, NEW YORK

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A New Process for the Preparation of Thioglycolylamides

BY JAMES A. VANALLAN

It is known that thioglycolylamides may be obtained by alkaline hydrolysis of carbamyl thioglycolylanilides¹ but the yields are low (15%) and several steps are required to obtain the product. Also acetothioglycolylamides, which are obtained from the acid chloride and an amine, may be saponified to the required thioglycolylamides but the intermediate acid chloride² is difficult to obtain, and again the process consists of several steps.

It has now been found that thioglycolylamides may be made in excellent yield and in a high state of purity without protecting the thiol group. The process consists of mixing an amine and thiogly-

colic acid in molecular proportions with benzene as a solvent and utilizing a Clarke-Rahrs ester column³ to remove the water as it is formed. The reactants are at all times in an atmosphere of benzene during the course of the reaction, which minimized the formation of disulfide. The crude product, therefore, usually possesses a higher degree of purity than that obtained by other processes. The process is illustrated by the preparation of thioglycolylanilide.

Thioglycolylanilide.—Thioglycolic acid (46 g.) and aniline (45 g.) are mixed in 250 ml. of benzene. This solution is refluxed, using an ester column, until approximately 9 ml. of water has separated (about nine hours). The benzene solution is then treated with an equal volume of petroleum ether and chilled. The product (70 g., 85%) separates as a mass of white crystals; m. p. 103-105°. A recrystallization from dilute alcohol raises the melting point to 110°.

(3) Eastman Kodak Company, "Syn. Org. Chem.," **9**, No. 3, May (1936).

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ROCHESTER 4, NEW YORK

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Resonance and Hydrogen Bond Effects on the Basic Strengths of Certain Arylalkyl Azomethines

BY CHARLES D. WAGNER AND EDWARD D. PETERS

When aliphatic primary amines are treated with most of the common aromatic aldehydes, azo-

(1) Beckurts and Frerichs, *J. prakt. Chem.*, [2] **66**, 174 (1902).

(2) Benary, *Ber.*, **46**, 2105 (1913).

methines are readily and quantitatively formed which ordinarily are considerably less basic than the aliphatic amines. This fact has been utilized as the basis of a method by which secondary plus tertiary aliphatic amines may be determined in the presence of primary amines and ammonia.¹

Reference has been made¹ to the fact that the titration of a mixture of an aliphatic secondary amine and the azomethine of a primary amine leads to the sharpest satisfactory differentiation between the two compounds when the azomethine is derived from salicylaldehyde. (Of benzaldehyde, *p*-hydroxybenzaldehyde, anisaldehyde, *o*-methoxybenzaldehyde, cinnamaldehyde, piperonal and *m*-nitrobenzaldehyde, the last-named formed an azomethine which was less basic than that derived from salicylaldehyde, but the compound formed was easily hydrolyzed in the presence of water and dilute acid and was therefore not used in the analytical method.)

Interesting differences were observed in the titration curves obtained by treating a mixture of di-*n*-amylamine and *n*-amylamine with different aromatic aldehydes and titrating in the usual way¹ using methanol as a solvent. Since benzaldehyde reacts to a significant extent with unsubstituted straight-chain secondary amines, the reaction time for benzaldehyde with the mixture was shortened to five minutes in comparison to twenty minutes used with the other aldehydes.

In each experiment 10 ml. of an isopropyl alcohol solution containing 1.80 millimoles of di-*n*-amylamine and 2.08 millimoles of *n*-amylamine was added to 80 ml. of methanol containing 40 millimoles of aldehyde (carboxylic acid-free). After the mixture stood at room temperature for twenty minutes, it was titrated potentiometrically, using 0.5 *N* hydrochloric acid in isopropyl alcohol.

Curves obtained using benzaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, anisaldehyde and *o*-methoxybenzaldehyde are presented in Fig. 1. From these it is noted that in the absence of phenolic aldehydes, the portions of the curves representing titration of secondary amine are almost identical. The phenolic aldehydes in the basic solutions cause decreased basicities corresponding to the relative acid strengths of the two aldehydes.

The portions of the curves representing titrations of azomethines demonstrate that azomethines from the methoxyaldehydes and *p*-hydroxybenzaldehyde are stronger bases (about 1 *pK* unit) than that from benzaldehyde, and about 1.5 *pK* units stronger than the azomethine from salicylaldehyde. These observations, which were confirmed qualitatively and almost quantitatively using the primary and secondary isobutylamines and isopropylamines, may be ascribed to resonance and hydrogen bond effects in the azomethines:

(1) C. D. Wagner, R. H. Brown, and E. D. Peters, 69, 2609 (1947).

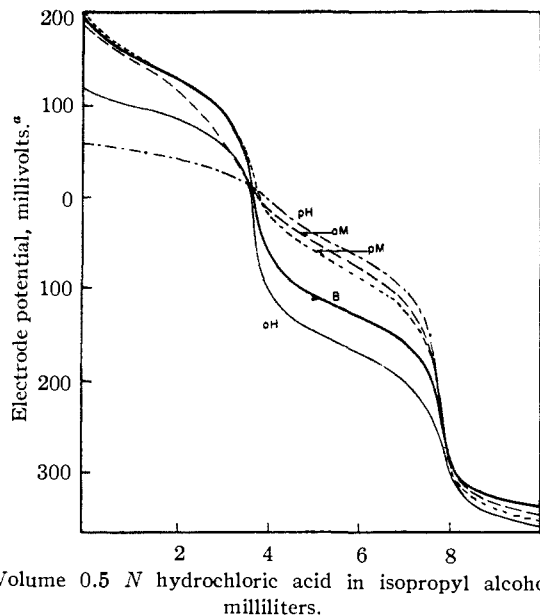
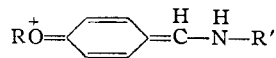


Fig. 1.—Acidimetric titrations of di-*n*-amylamine-*n*-amylamine mixtures in methanol after treatment with certain aromatic aldehydes: 1.8 milliequivalents of di-*n*-amylamine, 2.08 milliequivalents of *n*-amylamine treated with 40 millimoles of aldehyde in 80 ml. of methanol: —, B, benzaldehyde; —, oH, salicylaldehyde; —, pH, *p*-hydroxybenzaldehyde; —, oM, *o*-methoxybenzaldehyde; - - - - - , pM, anisaldehyde.

* Zero on electrode potential scale is approximately equivalent to a *pH* of 7 with the electrodes in aqueous solution.

1. Base strength of an azomethine from an ortho- or para-hydroxybenzaldehyde or *o*- or *p*-methoxybenzaldehyde tends to be increased over that of the benzaldehyde derivative because of the greater resonance energy of the conjugate acid of the azomethine, due primarily to the following resonance structure



where R equals either methyl or hydrogen and where the substituents may be either ortho or para.

2. The resonance effect in the case of the salicylaldehyde compound is more than compensated by hydrogen bonding between the ortho oxygen and the nitrogen atoms, which tends to decrease the basic character of the nitrogen atom of the azomethine so that the result is a compound somewhat less basic than the benzaldehyde derivative.

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