citral is a modification of the procedure of Fischer and co-workers.[2] A mixture of 11.7 g. (0.14 mole) of freshly distilled β-methylcrotonaldehyde, 1.5 ml. of glacial acetic acid and 0.15 ml. of piperidine was heated under nitrogen in a small Claisen flask on a steam-bath for twenty-three minutes. The reaction mixture turned very dark red almost at once and gradually thickened. After removing the flask from the steam-bath and cooling, a nitrogen filled capillary was inserted and the material was distilled at reduced pressure. In addition to some low boiling substance (unreacted β-methylcrotonaldehyde) which collected in a Dry Ice trap, three fractions were obtained: (1) b. p. 30–100° (2 mm.), wt. 0.7 g.; (2) b. p. 100–112° (2 mm.) (dark red), wt. 1.6 g.; (3) b. p. above 112° (2 mm.), bath temp. above 200°, wt. 0.5 g. The principal fraction (2) displayed a high sharp absorption spectra maximum at 338 mμ in 95% ethanol. Fraction (2) was treated directly with a slightly basic solution of 2 g. of cyanoacetic acid in 12 ml. of water and shaken vigorously for one-half hour during which time all of the oil dissolved. The basic aqueous solution was extracted three times with ether and acidified. A dark red oil appeared which crystallized at once to dark red shiny crystals. These were washed with water and dried; yield 1.82 g. A 300-mg. portion of these crystals was recrystallized three times from water–acetic acid yielding 149 mg. of pure dehydrocitrylidenecyanoacetic acid with the following physical properties: m. p. 195–198° (dec.), λ_{max} 390 mμ (ε 41200) in 95% ethanol. *Anal.* Calcd. for $C_{13}H_{15}O_2N$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.63; H, 6.99; N, 6.25. Quantitative catalytic hydrogenation showed 5.58 moles of hydrogen absorbed per mole. The compound contains four carbon–carbon double bonds and a nitrile group. In view of the unexpected hydrogenation result, quantitative hydrogenations were carried out on samples of very pure α-cyanocrotonic acid[7] which contains one carbon–carbon double bond and a nitrile group. This substance absorbed 2.73 and 2.57 moles of hydrogen per mole in duplicate experiments. This indicates that the nitrile group absorbs *ca.* 1.6 moles of hydrogen. Thus, the absorption of 5.58 moles of hydrogen by the dehydrocitrylidenecyanoacetic acid indicates the presence of four carbon–carbon double bonds.

Because of the large loss accompanying the formation of β-methylcrotonaldehyde from its diethyl acetal (usually 50–60% yield) and because of the large amount of side reaction loss attending the self-condensation of the aldehyde it was thought possible to perform the condensation using the acetal under conditions in which the aldehyde might be formed *in situ*. Attempts at such a reaction using, for example, wet acetic acid and piperidine failed. No dehydrocitral was obtained and usually 70–90% of the starting material could be recovered although it had been partially converted to the aldehyde.

Methyl Dehydrocitrylidenecyanoacetate.—The dry silver salt prepared from 1.52 g. of the dehydrocitrylidenecyanoacetic acid was refluxed and stirred with methyl iodide and ether for twenty-four hours. Evaporation of the ether after filtration and drying left 1.59 g. (98% yield) of methyl dehydrocitrylidenecyanoacetate. Recrystallization from methanol yielded a pure sample of the ester with the following physical properties: m. p. 115–118°, λ_{max} 405 mμ (ε 43300) in 95% ethanol. Molecular weight (in camphor)[8] was 235 ± 3, calcd. 231.

An attempt was made to condense β-cyclocitral with methyl dehydrocitrylidenecyanoacetate in a Knoevenagel type reaction. It was thought that some methyl axerophthylidenecyanoacetate might be formed in the reaction. Absorption spectrum measurements on the reaction mixture unfortunately failed to indicate unambiguously the presence or absence of the desired product. Molecular weight determinations,[8] however, indicated that perhaps the reaction had proceeded to a certain extent. A biological test performed with the purified reaction mixture failed to show any vitamin A activity.

(7) Young, Andrews, Lindenbaum and Cristol, THIS JOURNAL, **66**, 810 (1944).

(8) Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

β-Methylcrotonaldehyde.—Freshly distilled γ,γ-dimethylallyl bromide[6] ($n^{20}D$ 1.4900), 34.5 g. (0.23 mole), was added to a solution of hexamethylenetetramine in dry chloroform. The white precipitate which resulted was washed with ether and dried under vacuum. This salt was then dissolved in water and added dropwise to rapidly boiling water under a slow stream of nitrogen. The distillate was kept slightly acid by adding dilute sulfuric acid periodically. The distillate was extracted several times with ether and the combined ether extracts were dried over sodium sulfate. Removal of the ether and distillation of the residue through a small Vigreux column yielded 6.5 g. (0.078 mole, 35% yield) of β-methylcrotonaldehyde, b. p. 68–72° (95 mm.).

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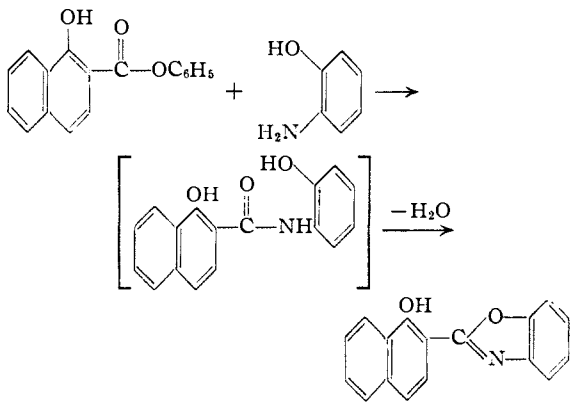
LOS ANGELES, CALIFORNIA RECEIVED MARCH 1, 1947

The Salol Reaction

BY JAMES A. VANALLAN

The "salol procedure"[1] is very convenient for preparing amides of salicylic acid, particularly from sensitive amines such as the aminophenols. By the use of the phenyl ester of 1-hydroxynaphthalene-2-carboxylic acid, homologs in the naphthalene series can be obtained. In the accompanying table there are listed the amines used with salol and with phenyl 1-hydroxynaphthalene-2-carboxylate (Table I), with the properties of the resulting compounds.

When the reaction is applied to *o*-aminophenols or *o*-diamines, a secondary loss of water gives rise to a cyclic compound instead of the open-chain amide.



In addition to the methods listed,[1] salicyl and hydroxynaphthoylamides have been prepared by the action of a dehydrating agent on mixtures of the acid and amine in an inert solvent[2,3,4,5]; from an aryl bromide and salicylamide[6,7]; from the anhydride of 2-hydroxy-3-naphthoic acid and an amine[8]; from 2-hydroxy-3-naphthoic acid and

(1) Allen and VanAllan, "Organic Syntheses," **26**, 94 (1946)
(2) Semer and Shepard, *J. Chem. Soc.*, **95**, 441 (1909).
(3) German Patent 293,897 (1913) [*Frdl.*, **12**, 912 (1914–1916)].
(4) German Patent 291,139 [*Frdl.*, **12**, 182 (1914–1916)].
(5) German Patent 284,997 [*Frdl.*, **12**, 183 (1914–1916)].
(6) Loevenich and Loeser, *Ber.*, **60**, 322 (1927).
(7) Goldberg, *ibid.*, **39**, 1691 (1906).
(8) German Patent 295,183 [*Frdl.*, **12**, 914 (1914–1916)].

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.	% Nitrogen 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
n-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	$C_{16}H_{16}N_2O_4$	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]
o-Aminophenol	125	22.4	$C_{13}H_9NO_2$	6.63[e]	6.63[e]
p-Aminophenol[12]	176	57			
m-Aminophenol	184	58	$C_{13}H_{11}NO_2$	6.11	6.10
5-Aminoindazole	230	37	$C_{14}H_{11}N_3O_2$	16.62	16.57
6-Aminoindazole	234–235	31	$C_{14}H_{11}N_3O_2$	16.62	16.56
m-Phenylenediamine[12]	199–200	49			
5-Aminobenzotriazole	245	42	$C_{13}H_{10}N_4O_3$	22.03	21.74
1,2,3,4-Tetrahydroquinoline	138–139	34	$C_{16}H_{15}NO_2$	5.5	5.6
		With Phenyl-1-hydroxynaphthalene-2-carboxylate			
Diethylamine	[f]	63	$C_{15}H_{17}NO_2$	5.77	5.6
o-Phenylenediamine	>265	78	$C_{17}H_{12}N_2O$	[g]	[g]
o-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.

acetanilide[9] or aniline[10], from methyl salicylate and an aliphatic amine.[11,12]

(9) German Patent 289,027 [*Frdl.*, **12**, 184 (1914–1916)].
(10) Schöpff, *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 RECEIVED JULY 10, 1947

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 thioglycolylanilides[1] 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 chloride[2] 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 thioglycolic acid in molecular proportions with benzene as a solvent and utilizing a Clarke–Rahrs ester column[3] 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°.

(1) Beckurts and Frerichs, *J. prakt. Chem.*, [2] **66**, 174 (1902).
(2) Benary, *Ber.*, **46**, 2105 (1913).
(3) Eastman Kodak Company, "Syn. Org. Chem.," **9**, No. 3, May (1936).

COMMUNICATION NO. 1156
KODAK RESEARCH LABORATORIES
ROCHESTER 4, NEW YORK RECEIVED JULY 26, 1947

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-