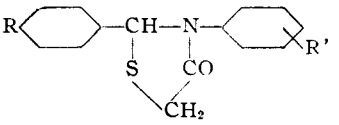
TABLE I

2,3-SUBSTITUTED-4-THIAZOLIDONES



R	R'	Reflux time, hr.	Yield,[a] %	Recryst. solvent	M. p., °C. (corr.)	Analyses, %[b] Nitrogen Calcd.	Nitrogen Found	Sulfur Calcd.	Sulfur Found
H	H	4	60	Benzene–ether	131.6–132.2[c]	5.49	5.37	13.55	12.63
H	3-Cl	[d]	38	Methanol	128.6–129.6	4.84	4.76	11.05	11.05
H	4-Cl	12	50	Benzene	110.8–112.2	4.84	4.59	11.05	10.80
H	2-OH	8	66	Ethanol	222–224	5.17	5.07	11.80	12.03
H	4-OH	6	61	Ethanol	191.8–193	5.17	5.10	11.80	11.94
H	3-COOH	12	63	Isopropanol	186.5–188	4.68	4.61	10.7	11.0
H	4-COOH	17	25	Isopropanol	244–245.1	4.68	4.65	10.7	10.70
H	4-$COOC_2H_5$	15	28	Benzene–ether	126.8–128.8	4.28	4.20	9.79	9.88
OCH_3	4-OCH_3	12	52	Methanol	118.9–119.8	4.44	4.47	10.16	9.96

[a] No attempt was made to obtain maximum yields, since our interest was chiefly in the scope of the reaction. [b] Analyses were performed by the analytical staff of these Laboratories. [c] Erlenmeyer and Oberlin report a m. p. 130–131°. [d] Reaction carried out at room temperature for five days.

usually approached the theoretical. After most of the benzene had been removed, the residue was dissolved in ether and seeded. In some instances, the thiazolidone separated directly from the benzene solution and was filtered off and purified by recrystallization.

Reaction of Thioglycolic Acid with Benzylidene-2-carboxyaniline.—Five grams of thioglycolic acid was added to a well-stirred suspension of 11.3 g. of benzylidene-2-carboxyaniline in 75 cc. of benzene. An exothermic reaction occurred and a clear solution resulted. The product which precipitated in a matter of a few minutes proved to be the addition compound. After several recrystallizations from a mixture of ether-Skellysolve A, it melted at 101–102°.

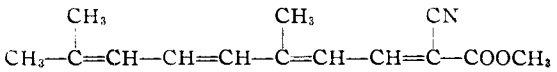
Anal. Calcd. for $C_{16}H_{15}NO_4S$: S, 10.1. Found: S, 9.96.

STERLING-WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK RECEIVED SEPTEMBER 23, 1947

Polyenes. VI. Methyl Dehydrocitrylidenecyanoacetate[1]

BY WILLIAM G. YOUNG AND SEYMOUR L. LINDEN

For a research program which was later abandoned we wished to prepare dehydrocitrylidenecyanoacetate (I) from dehydrocitral and cyano-



I

acetic acid followed by esterification. Dehydrocitral has been prepared previously[2] by the self condensation of β-methylcrotonaldehyde. The isolation of the dehydrocitral and its separation from isomers and other condensation products, however, is accomplished only by tedious redistillations and recrystallizations. Fortunately, for the purpose of this investigation it was found unnecessary to carry out such purifications since treatment of the main fraction from the condensation reaction with a basic aqueous solution of cyanoacetic acid yielded directly pure crystalline dehydrocitrylidenecyanoacetic acid. The methyl ester was then prepared by treatment of the silver salt of the acid with methyl iodide.

The absorption spectra of dehydrocitrylidenecyanoacetic acid (λ_{max} 390 mμ, ε 41200) and its methyl ester (λ_{max} 405 mμ, ε 43300) correspond well in both wave length and extinction with that expected of a new group of alkylidenecyanoacetic acid and esters with four conjugated carbon–carbon double bonds.[3]

The usual procedure for the preparation of β-methylcrotonaldehyde[4] *via* α-bromoisovaleraldehyde diethyl acetal (followed by dehydrobromination and hydrolysis of the acetal) was found by us to be both time consuming and expensive. The over-all yield from isovaleraldehyde is seldom better than 10%. We have found, on the other hand, that β-methylcrotonaldehyde can be prepared readily from γ,γ-dimethylallyl bromide by the method of Sommelet.[5] The γ,γ-dimethylallyl bromide is conveniently prepared in large quantities by the addition of hydrogen bromide to isoprene.[6] The reaction of the bromide with hexamethylenetetramine is almost quantitative and the decomposition of the salt thus obtained is readily carried out by steam distillation. The yield from the allylic bromide is 35%.

We wish to thank Mr. Joseph Rule for the preparation of the γ,γ-dimethylallyl bromide. The micro-analyses reported were carried out at the California Institute of Technology through the courtesy of Professor Haagen-Smit.

Experimental

Dehydrocitral and Dehydrocitrylidenecyanoacetic Acid.—The process employed for the preparation of dehydro-

(1) This work was made possible by a research grant from Sharp and Dohme, Inc.

(2) Fischer and Hultzsch, *Ber.*, **68**, 1726 (1935); Fischer, Hultzsch and Plaig, *ibid.*, **70**, 370 (1937).

(3) Andrews, Cristol, Lindenbaum and Young, THIS JOURNAL, **67**, 715 (1945).

(4) McElvain, Clarke and Jones, *ibid.*, **64**, 1966 (1942); Fischer, Ertel and Lowenberg, *Ber.*, **64**, 30 (1931).

(5) Sommelet, *Compt. rend.*, **157**, 852 (1933); Delaby, *Bull. soc. chim.*, [5] **3**, 2375 (1936).

(6) Staudinger, Kries and Schilt, *Helv. Chim. Acta*, **5**, 743 (1922).

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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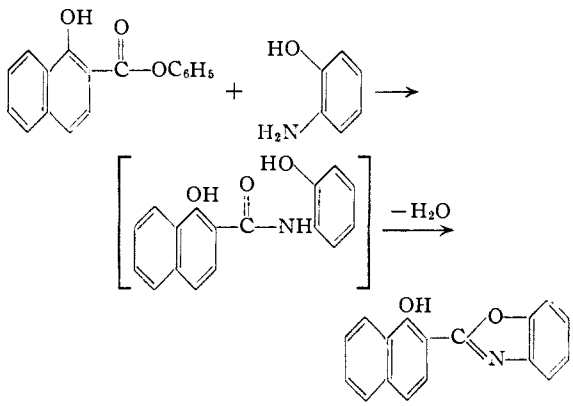
LOS ANGELES, CALIFORNIA RECEIVED MARCH 1, 1947

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)].