TABLE I

YIELDS AND CONSTANTS OF HYDROCARBAZOLES

| | | | Analyses, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calculated | | | | Found | | | |
| Carbazoles | % Yield, crude | M. p., °C. (cor.) | C | H | N | Mol. wt. | C | H | N | Mol. wt. |
| 1,2,3,4-Tetrahydro-[a] | 88[d]–95[e] | 117–118 | 84.2 | 7.7 | 8.2 | 171 | 84.2 | 8.0 | 8.5 | 170 |
| 2-Methyl-1,2,3,4-tetrahydro-[b] | 65[d] | 98–100[g] | 84.3 | 8.2 | 7.6 | 185 | 84.2 | 8.6 | 7.2 | 190 |
| 3-Methyl-1,2,3,4-tetrahydro-[b] | 70[d] | 108–111[h] | 84.3 | 8.2 | 7.6 | 185 | 84.3 | 8.0 | 7.5 | 184 |
| 2,4-Dimethyl-1,2,3,4-tetrahydro-[a] | 60[d] | 103–106[i] | 84.4 | 8.6 | 7.0 | 199 | 84.2 | 8.6 | 7.0 | 202 |
| 1,2-Benzo-3,4-dihydro-[a] | 80[d] | 163–164[j] | 87.6 | 6.0 | 6.4 | 219 | 87.7 | 5.8 | 6.8 | 217 |
| 6-Nitro-1,2,3,4-tetrahydro-[c] | 60[f] | 169–172[k] | 66.7 | 5.6 | 13.0 | 216 | 66.7 | 5.2 | 12.8 | 221 |

[a] From methyl alcohol. [b] From methyl alcohol or cyclohexane. [c] Red-brown crystals from 95% ethyl alcohol. [d] Acetic acid method. [e] Alcohol–hydrochloric acid method. [f] Aqueous mineral acid method; contaminated by *p*-nitrophenylhydrazone. [g] Borsche, *Ann.*, **359**, 62 (1908), reported 94° as m. p.; Plancher and Carrasco, *Atti. accad. Lincei*, [5] **13**, I, 632 (1904), reported 98–99°. [h] Plant and Rosser, *J. Chem. Soc.*, 2454 (1928). [i] Braun and Haensel (*Ber.*, **59**, 1999 (1926)) reported m. p. to be 96–99°; their product was red, ours was faintly yellow. [j] Ghigi, *Gazz. chim. ital.*, **60**, 194 (1930). [k] Borsche, *Ann.*, **359**, 49 (1908).

The alcohol–mineral acid method produced the *p*-nitrophenylhydrazone of cyclohexanone (m. p. 144–145°), which was converted to 6-nitro-1,2,3,4-tetrahydrocarbazole by boiling with 10% sulfuric acid according to the directions of Borsche.[5]

**Purification of Hydrocarbazoles.**—It has been reported that tetrahydrocarbazole quickly turns yellow-brown in the air and that it has a fecal odor.[6] We fractionally crystallized tetrahydrocarbazole from methyl alcohol and obtained a colorless, odorless product which was unchanged on standing three months in air and light. 1,2-Benzo-3,4-dihydrocarbazole was also easily purified, but the methyl-substituted tetrahydrocarbazoles became yellowish upon removal from the solvent, although the analytical values were satisfactory.

**Freezing and Melting Points of 1,2,3,4-Tetrahydrocarbazole.**—Four successive cooling curve determinations were made on a sample of highly purified tetrahydrocarbazole. The slope of the first plateau was zero within the accuracy of the determination, but the slopes of the subsequent plateaus became successively greater. The extrapolated freezing points were 118.4, 117.2, 115.4 and 111.7°, respectively. Purified tetrahydrocarbazole showed a capillary melting point (cor.) of 117–118° with the usual rate of heating; but with slow heating (1° per min.), the melting point was 113–114°, and the sample started to soften at 109°.

(5) Borsche, *Ann.*, **359**, 52 (1908).

(6) Zanetti, *Ber.*, **26**, 2006 (1893).

MULTIPLE FELLOWSHIP ON TAR SYNTHETICS
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# The Preparation of 4-Thiazolidones by the Reaction of Thioglycolic Acid with Schiff Bases

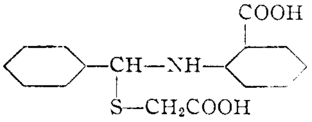
BY ALEXANDER R. SURREY

The appearance of a paper by Erlenmyer and Oberlin[1] on the reaction of Schiff bases with thioglycolic acid prompts the writer to report on similar work in this field carried out in this Laboratory.

We have found that in many instances 4-thiazolidones (Table I) can be prepared conveniently by the reaction of thioglycolic acid with Schiff bases in refluxing benzene. By removing the water continuously as it forms, it was possible to follow the condensation and determine the reaction time. In some cases the Schiff base was prepared in the same solvent. When the calculated amount of water had separated, the thioglycolic acid was added and refluxing was continued. The initial step, the addition of the thiol group to the anil, was usually accompanied with the evolution of heat. Where the Schiff base was only slightly soluble in benzene, vigorous mechanical stirring was employed.

Several other procedures were tried in the preparation of 2,3-diphenyl-4-thiazolidone. At room temperature, in the absence of solvent a 35% yield of the product was obtained; in alcohol or glacial acetic acid, the yield was 12%. The reaction of ethyl thioglycolate with benzylideneaniline in refluxing Skellysolve E for sixteen hours gave an 8% yield of the thiazolidone.

When thioglycolic acid was added to a stirred suspension of benzylidene-2-carboxyaniline in benzene an exothermic reaction occurred and a clear solution resulted. In a short time, a solid which proved to be the addition compound, separated from the benzene solution. When the reaction was run in refluxing benzene for twenty-four hours, approximately 75% of the calculated amount of water was collected. Although thiazolidone formation is indicated, the product has not yet been isolated from the reaction mixture.



## Experimental Part[2]

**General Procedure for the Preparation of the 4-Thiazolidones.**—The following general directions for the preparation of the thiazolidones (Table I) includes the procedure for the preparation of the Schiff base in the same solvent. A mixture of 0.2 mole of benzaldehyde and 0.2 mole of aniline in 100 cc. of dry benzene was refluxed with a water separator connected to the apparatus. After about 3.5 cc. of water had been collected, 20 g. of thioglycolic acid was added and refluxing continued until an additional 3.5 cc. of water had separated. The amount of water collected

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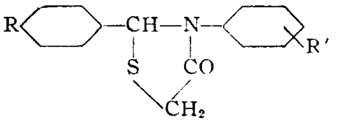
(1) Erlenmyer and Oberlin, *Helv. Chim. Acta*, **30**, 1329 (1947).

(2) All melting points are uncorrected unless otherwise indicated.

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 | 12.55 | 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.

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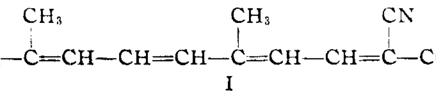
## Polyenes. VI. Methyl Dehydrocitrylidenecyanoacetate[1]

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-



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH=CH-\overset{CH_3}{\overset{|}{C}}=CH-CH=\overset{CN}{\overset{|}{C}}-COOCH_3$$

I

acetic acid followed by esterification. Dehydrocitral has been prepared previously[2] by the self condensation of $\beta$-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 ($\lambda_{max}$ 390 m$\mu$, $\epsilon$ 41200) and its methyl ester ($\lambda_{max}$ 405 m$\mu$, $\epsilon$ 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 $\beta$-methylcrotonaldehyde[4] *via* $\alpha$-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 $\beta$-methylcrotonaldehyde can be prepared readily from $\gamma,\gamma$-dimethylallyl bromide by the method of Sommelet.[5] The $\gamma,\gamma$-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 $\gamma,\gamma$-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-

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[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 Flaig, *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).