thorium nitrate according to the modified procedure of Armstrong.[3]

Summary

Six 9,10-diaryldihydrophenanthrenediols have been synthesized.

9,9-Diarylphenanthrones are formed by rearrangement of the pinacols.

The 9,9-diarylphenanthrones are cleaved into 2-(diarylmethyl)-2′-carboxylbiphenyls by fusion with potassium hydroxide.

The diaryldihydrophenanthrenediols are oxidized to 2,2′-diacylbiphenyls by chromic acid.

(3) Armstrong, THIS JOURNAL, **55**, 1741 (1933).

ANN ARBOR, MICHIGAN RECEIVED APRIL 8, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BUREAU OF DAIRY INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Addition of Mercaptans to Certain Double Bonds

BY BEN H. NICOLET

Some time ago the writer reported[1,2] the ready addition of *p*-tolylmercaptan to certain rather reactive double bonds (in α,β-unsaturated ketones and esters) in the presence of sodium alcoholates. More recently, the sodium salt of benzalpyruvic acid proved so insoluble that the addition of mercaptans could not be carried out by this method.

It was, however, noted that Kohler[3] had found that sulfinic acids sometimes add to unsaturated ketones as such, without the addition of alkali. The corresponding experiment with mercaptans was most successful. Benzalacetophenone and either *p*-tolyl or benzyl mercaptan, when heated together on the water-bath without any catalyst, showed quite complete reaction in five minutes, though *not* in two minutes. The product was, as expected, $PhCH(SR)CH_2COPh$, where R was either *p*-tolyl or benzyl. The corresponding addition of these mercaptans to benzalpyruvic acid, PhCH=CHCOCOOH, occurs about equally readily.

The addition of hydrogen sulfide to unsaturated ketones of this type has been reported in the presence of alkali as weak as sodium carbonate in alcohol suspension.[4] The writer has, however, found that hydrogen sulfide adds readily to benzalacetophenone in alcohol without even this amount of alkali.

Methyl cinnamate also presents a double bond of somewhat (although decidedly less) enhanced reactivity. Without catalyst, the addition of either of the mercaptans mentioned was doubtful after five hours at 100°. With the addition, however, of 0.1 cc. of piperidine for 5 g. of ester, a good yield was obtained after two hours (but *not* after half an hour) at 100°.

Additions of these mercaptans to α-acetylaminoacrylic acid, and to other aminoacrylic acid derivatives, are being reported elsewhere, in connection with a new synthesis of cystine which may have biological significance. The work described was undertaken primarily to throw light on the probability of the assumption of an addition of hydrogen sulfide or methyl mercaptan to methylenepyruvic acid, CH_2=CHCOCOOH (as yet unknown), as an early stage in a possible biological synthesis of methionine and homocystine. This point will be discussed further in another place.

On reëxamination of the literature, after completion of the work reported, it seems proper to call attention to the almost incredible reactivity of thioglycolic acid found by Holmberg,[5] and also to the unsaturated mercaptans of v. Braun and Plate,[6] which polymerize on standing.

Experimental Part

β - Phenyl - β - benzylmercaptopropiophenone.—Equimolecular quantities of benzalacetophenone and benzylmercaptan were mixed and heated for five minutes on the steam-bath. A good yield of pure product (m. p. 71°) was obtained after crystallization from alcohol. A reaction time of two minutes gave a much poorer yield.

Anal. (Parr bomb) Calcd. for $C_{22}H_{20}OS$: S, 9.64. Found: S, 9.78, 9.84.

Under similar conditions, but using *p*-tolylmercaptan, altogether similar results were obtained. The known β-phenyl-β-*p*-tolylmercaptopropiophenone was obtained, m. p. 113°.[1]

(1) Nicolet, THIS JOURNAL, **53**, 3066 (1931).
(2) Nicolet, *J. Biol. Chem.*, **95**, 389 (1932).
(3) Kohler and Reimer, *Am. Chem. J.*, **31**, 163 (1904).
(4) See Hooper, Macbeth and Price, *J. Chem. Soc.*, 1147 (1934), for a summary of the literature.
(5) Holmberg, *Ber.*, **65**, 1349 (1932); Axberg and Holmberg, *ibid.*, **66**, 1193 (1933).
(6) V. Braun and Plate, *ibid.*, **67**, 281 (1934).

α-Keto-γ-p-tolylmercapto-γ-phenylbutyric Acid.—Two grams of benzalpyruvic acid was heated with one mole of *p*-tolylmercaptan for ten minutes (steam-bath). The product was dissolved in 10 cc. of benzene, and a considerable amount of petroleum ether (Skellysolve F) added. An oil precipitated at once, which, when properly seeded, crystallized nicely. When not seeded, some days of standing was at times necessary. A good yield was obtained of a product which, after three similar crystallizations, melted at 97–98°.

Anal. (Parr bomb) Calcd. for $C_{17}H_{16}O_3S$: S, 10.67. Found: S, 10.69, 10.75.

α-Oximino-γ-p-tolylmercapto-γ-phenylbutyric Acid.—One gram of the keto acid and 0.3 g. each of hydroxylamine hydrochloride and sodium acetate were heated in 10 cc. of alcohol for an hour. After several recrystallizations from somewhat diluted alcohol, the oxime melted at 160°.

Anal. (Parr bomb) Calcd. for $C_{17}H_{17}O_3NS$: S, 10.15. Found: S, 10.11, 10.32.

α-Oximino-γ-benzylmercapto-γ-phenylbutyric Acid.—Benzalpyruvic acid and benzylmercaptan were condensed as described above. As the product failed to crystallize, it was converted directly to the oxime. This was obtained by precipitation from benzene with petroleum ether as a solid the crystalline character of which was rather doubtful. It melted at 95–97°.

Anal. (Parr bomb) Calcd. for $C_{17}H_{17}O_3NS$: S, 10.15. Found: S, 10.33, 10.40.

Methyl β-Phenyl-β-p-tolylmercaptopropionate.—Equimolecular quantities of methyl cinnamate and *p*-tolylmercaptan were heated (steam-bath) for periods up to five hours. Little reaction had, apparently, taken place in any case. With the addition of 0.1 cc. of piperidine, the reaction was very incomplete in half an hour, but after two hours, a good yield of the addition product was obtained, m. p. 59–60°.

Anal. (Parr bomb) Calcd. for $C_{17}H_{18}O_2S$: S, 11.19. Found: S, 11.16, 11.31.

Ethyl α-Benzoylamino-β-phenyl-β-benzylmercaptopropionate.—Four grams of ethyl α-benzoylaminocinnamate, 1 mole of benzylmercaptan, and 0.1 cc. of piperidine in 10 cc. of absolute alcohol gave after five hours of refluxing followed by crystallization from diluted alcohol, 3.5 g. of the above ester of m. p. 119–120°.

Anal. (Parr bomb) Calcd. for $C_{25}H_{25}O_3NS$: S, 7.64. Found: S, 7.82, 7.81.

Summary

1. The addition of benzyl- and *p*-tolylmercaptans to α,β-unsaturated ketones takes place very readily at 100° without catalysts.

2. Similar additions to α,β-unsaturated esters occur rather less readily, and in the presence of piperidine.

3. The relation of these facts to the natural synthesis of methionine will be discussed elsewhere.

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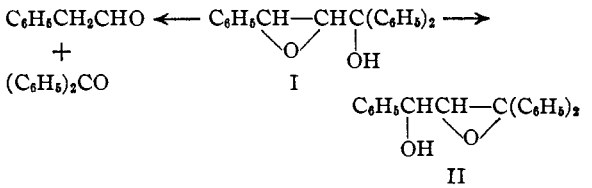
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Properties of Certain Beta Oxanols

BY E. P. KOHLER AND C. L. BICKEL

An earlier paper from this Laboratory[1] contains a description of the peculiar properties of a β-oxanol which under certain conditions is cleaved and under others that are not very different is rearranged to an isomer.



As a result of further study it is possible now to define more sharply the conditions under which these transformations occur and to exclude some of the mechanisms that were suggested.

The cleavage is dependent on the replacement of the hydrogen of the hydroxyl group with a metal. By treating the oxanol at low temperatures with Grignard reagents, lithium organic compounds, or sodium in liquid ammonia it is possible to convert it into metallic derivatives from which it is regenerated by acids. At higher temperatures all these metallic derivatives decompose into benzophenone and the corresponding metallic derivatives of the aldehyde. This cleavage is quite general for β-oxanols; by similar treatment the isomeric oxanol II is cleaved into benzaldehyde and a metallic derivative of diphenyl acetaldehyde.

In contrast with cleavage the rearrangement from one oxanol to another can be effected catalytically. It is induced by methyl alcoholic solutions of small quantities of alkaline hydroxides, alkaline carbonates, barium oxide, magnesium methylate and tetramethylammonium hydroxide, but not by acetates, ammonia, pyridine and piperidine. In the cases which have been investigated it is not reversible.

(1) Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 205 (1931).