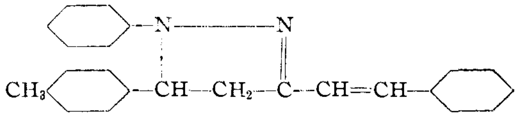
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Effect of Constitution on the Rearrangement of the Phenylhydrazones of Some Unsymmetrically Substituted Dibenzalacetones[1]

BY L. CHAS. RAIFORD AND EDWARD L. HILL

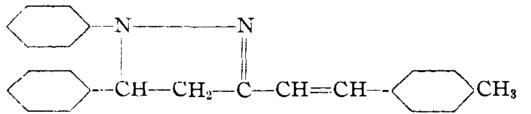
In a recent report from this Laboratory[2] there was described work on the rearrangement of the phenylhydrazones of certain unsymmetrically substituted[3] dibenzalacetones to the isomeric pyrazolines. Oxidation of the latter gave 1,5-diphenylpyrazole-3-carboxylic acid and benzoic or a substituted benzoic acid, indicating that the closing of the pyrazoline ring involved the unsaturation farthest from the nucleus bearing the "acid-forming" substituent. The present paper deals with the behavior of compounds containing "non-acidic" groups, *viz.*, alkyl, alkoxyl and alkylamino radicals.

Treatment of styryl 4-methylstyryl ketone with phenylhydrazine gave a product that could not be reduced by sodium amalgam, that suffered no change when boiled with acetic acid, and which was regarded as a pyrazoline. Analyses for starting material and product (see Tables I and II) agree with 1-phenyl-3-styryl-5-(4-methylphenyl)-pyrazoline, with structure A



A

and with 1-phenyl-3-(4-methylstyryl)-5-phenylpyrazoline, of structure B



B

Oxidation of the compound, as described below, gave benzoic and terephthalic[4] acids which did not distinguish between the two possible structures. The compound obtained from phenylhydrazine and di-(4-methylstyryl) ketone also appeared to be a pyrazoline.[5] When this was oxidized only terephthalic acid could be isolated.

The compounds obtained when styryl 4-methoxy-, 4-ethoxy-, 4-propoxy- and methylene-3,4-dioxystyryl ketones reacted with phenylhydrazine likewise failed to respond to tests for hydrazones, and were probably pyrazolines. Oxidation gave, in the first two cases, benzoic and the pyrazole acids required by structure A. In the last case, oxidation of several portions always gave benzoic acid, which indicated structure A. When the product obtained from di-(methylene-3,4-dioxystyryl) ketone was oxidized, no acid could be isolated, which indicated complete degradation.[6]

The action of phenylhydrazine on styryl 4-dimethylaminostyryl ketone gave a product that was regarded as a hydrazone. While it could not be reduced by sodium amalgam it was rearranged by boiling acetic acid. It was also hydrolyzed by sulfuric acid and the presence of phenylhydrazine in the reaction mixture was established by oxidation with Fehling's solution. Although the volume of nitrogen obtained (see experimental part) was little more than one-half that required by theory, the fact that none was liberated when the corresponding rearranged product was subjected to the same treatment clearly indicated that the first compound was a hydrazone.[7]

Experimental Part

Preparation of the Ketones.—To a solution of 30 g. of benzalacetone and the necessary amount of the required aldehyde in 1800 cc. of 50% alcohol, 60 cc. of 10% solution of sodium hydroxide was slowly added with stirring, the mixture stirred for two hours longer, and then allowed to stand at room temperature for twelve hours. The solid

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[1] Abstract of a portion of the thesis submitted by Edward L. Hill in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Iowa.

[2] Raiford and Entrikin, THIS JOURNAL, **55**, 1125 (1933).

[3] The substituents were halogen and the nitro group.

[4] Identified as the dimethyl ester, m. p. 139–140°. Schwanert [*Ann.*, **132**, 269 (1864)] found 140°.

[5] *Anal.* Calcd. for $C_{25}H_{24}N_2$: N, 7.95. Found: N, 8.15.

[6] It has been shown [THIS JOURNAL, **55**, 1127 (1933)] that oxidation of these pyrazolines gives acids that are themselves further attacked by permanganate under the conditions.

[7] Strache [*Monatsh.*, **12**, 528 (1891)] found that hydrazones of aldehydes and ketones, including osazones, fail to reduce Fehling's solution, but that phenylhydrazine does so at the boiling point with the liberation of all nitrogen. Hydrolysis of this type of product by means of acids, however, is seldom quantitative [Sidgwick, "Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1910, p. 247]. Francesconi and Milesi [*Gazz. chim. ital.*, **32**, 425 (1902)] found that treatment of acetoxime with hydrochloric acid gave an equilibrium mixture in which about one-third of the oxime had been decomposed. Also, Teeters and Shriner [THIS JOURNAL, **55**, 3028 (1933)] showed that the β-oxime of triketohydrindene could be refluxed with 35% sulfuric acid without hydrolysis, while Fischer and Jourdan [*Ber.*, **16**, 2243 (1883)] obtained a hydrazone that suffered no change when boiled with dilute hydrochloric or sulfuric acid. In addition, the attempt to hydrolyze the product here in question may have rearranged part of it to pyrazoline, which is not oxidized by Fehling's solution.

that separated was collected, washed with water to remove alkali, with dilute alcohol, and finally crystallized from a suitable solvent. Data for the new ones are given in Table I.

TABLE I

UNSYMMETRICAL DISTYRYL KETONES (SOLVENT, ALCOHOL)

Substituted styryl	Yield,[a] %	M. p., °C.	Formula	Crystal form	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
4-Methyl-	67	107–108	$C_{18}H_{16}O$	Light yellow needles	87.09	86.91	6.45	6.34
4-Ethoxy-	68	77–78	$C_{19}H_{18}O_2$	Yellow flakes	82.01	81.92	6.47	6.57
4-Propoxy-	60	119–120[b]	$C_{20}H_{20}O_2$	Pale yellow flakes	82.19	82.07	6.85	6.96

[a] Represents purified material. [b] Mixtures of this product with benzoic acid, m. p. 121°, and dibenzalacetone, m. p. 112°, respectively, melted in each instance with pronounced depression.

Phenylhydrazone of Styryl 4-Dimethylaminostyryl Ketone.—To a solution of 26 g. of the required ketone[8] in 2000 cc. of glacial acetic acid, 11.4 g. of phenylhydrazine was slowly added with stirring and the mixture allowed to stand at room temperature for twenty-four hours. The liquid standing above the few rosets of needles that had separated was decanted and to it was added methyl alcohol[9] until precipitation started and the mixture allowed to stand for another day. The solid was removed, washed with 15 cc. of ethyl acetate and obtained in yellow needles; m. p. 162–163; yield, 52%.

Anal. Calcd. for $C_{25}H_{25}N_3$: N, 11.44. Found: N, 11.46.

Attempts to reduce this product with sodium amalgam by Tafel's[10] method were unsuccessful. A portion of the phenylhydrazone was digested with 5 cc. of concentrated sulfuric acid for several hours at room temperature. The mixture was then transferred to one of the flasks (A) used in a modified form of the apparatus described by Frerichs and Mannheim[11] in which bottle C and tube D were replaced by two flasks that were connected by two sealed-in glass tubes. The upper tube connected the necks of the flasks a few centimeters below their mouths, while the lower one joined the bulbs just below the shoulders, so that liquid could readily be transferred from one flask to the other by "tipping" the apparatus. The mouth of one flask (A) was closed, and that of the other (B) was connected to a nitrometer. Fehling's solution was placed in (B), the pressure adjusted and the nitrometer read. The reagent was heated to boiling, the hydrolysis mixture from flask (A) transferred to B, the whole allowed to come to room temperature and the new volume read.

Anal. Subs., 0.5000: 18.8 cc. N. Calcd. for $C_{25}H_{25}N_3$: N, 30.5 cc.

1 - Phenyl - 3 - styryl - 5 - (4 - dimethylaminophenyl)-pyrazoline.—The above described hydrazone was rearranged by heating it under reflux for one hour with glacial acetic acid. The solution became green and deposited a greenish-yellow solid on cooling. Substitution of benzene for acetic acid gave an intensely greenish-yellow fluorescent product. Recrystallization from acetic acid or benzene gave yellow needles; m. p. 133–134°. This product gave no gas when treated with sulfuric acid and Fehling's solution as indicated above.

Anal. Calcd. for $C_{25}H_{25}N_3$: C, 81.74; H, 6.81. Found: C, 81.76; H, 6.71.

TABLE II

SUBSTITUTED 1-PHENYL-3-STYRYLPYRAZOLINES

Radical in position 5	Solvent	Crystal form	Formula	M. p., °C.	Analyses, nitrogen, % Calcd.	Analyses, nitrogen, % Found
4-Dimethylaminophenyl-	Alc.	Yellow needles	$C_{18}H_{21}N_3$	166–167	15.05	14.97
p-Tolyl-	Alc.	Yellow needles	$C_{24}H_{22}N_2$	167–168	8.28	8.21
4-Methoxyphenyl-[a]	EtOAc	Yellow prisms	$C_{24}H_{22}ON_2$	124	7.91	7.91
4-Ethoxyphenyl-	EtOAc	Yellow prisms	$C_{25}H_{24}ON_2$	126–127	7.61	7.58
4-Propoxyphenyl-	EtOAc	Greenish-yellow prisms	$C_{26}H_{26}ON_2$	118–119[b]	7.33	7.17
Methylene-3,4-dioxyphenyl-[c]	EtOAc	Amber prisms	$C_{24}H_{20}O_2N_2$	167–168	7.61	7.48

[a] The starting ketone used here was obtained in yellow needles that melted at 96–97°. Baeyer and Villiger [*Ber.*, **35**, 3022 (1902)] recorded 96.5° for a product that separated as an oil and later solidified. In the present work no oil was noted. [b] A mixture of this and the starting ketone, m. p. 119–120°, showed a melting range of 100–108°. [c] The ketone used here was prepared in 75% yield as directed by Kostanecki and Maron [*Ber.*, **31**, 728 (1898)] and obtained in yellow needles, m. p. 115°. The previous authors recorded no yield.

The product obtained by treatment of *p*-dimethylaminobenzalacetone with phenylhydrazine was crystallized from ethyl acetate in yellow needles with a greenish fluorescence; m. p. 166–167°. Boiling acetic acid caused no change and indicated a pyrazoline.

Anal. Calcd. for $C_{18}H_{21}N_3$: N, 15.05. Found: N, 14.97.

Data for other pyrazolines are given in Table II.

Oxidation of the pyrazolines was conducted as previously described with the exception that a more dilute solution of oxidizing agent was used and the temperature

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[8] The purified product was obtained in 46% yield by following Borsche [*Ann.*, **376**, 177 (1910)].

[9] Addition of water at this stage to cause separation of product often gave resinous material.

[10] Tafel, *Ber.*, **22**, 1854 (1889).

[11] Frerichs and Mannheim, *Arch. Pharm.*, **256**, 112 (1918).

was kept between 80 and 90°. Data for the acids obtained are given in Table III.

TABLE III

SUBSTITUTED 1,5-DIPHENYLPYRAZOLE-3-CARBOXYLIC ACIDS (COLORLESS PRISMS FROM ALCOHOL)

Substituted phenyl in position 5	Formula	M. p., °C.	Analyses, nitrogen, % Calcd.	Analyses, nitrogen, % Found
4-Methoxy-	$C_{17}H_{14}O_3N_2$	196–197[a]	9.52	9.46
4-Ethoxy-	$C_{18}H_{16}O_3N_2$	163–164	9.09	8.91
4-Dimethylamino-	$C_{18}H_{17}O_2N_3$	141–142[b]	13.68	13.50

[a] This product was further identified by comparison with the acids obtained by oxidation of 1-phenyl-3-(4-methoxystyryl)-5-(4-methoxyphenyl)-pyrazoline, first obtained by Straus [*Ber.*, **51**, 1471 (1918)]. A mixture of one of them, shown to be anisic acid, m. p. 184°, with the product here in question, had a melting range of 140–145°; with the other one, m. p. 196–197°, no depression was noted; with 1,5-diphenylpyrazole-3-carboxylic acid, m. p. 185°, the range was 160–165°. [b] This acid was also obtained by oxidation of 1-phenyl-3-methyl-5-(4-dimethylaminophenyl)-pyrazoline.

Summary

1. Several unsymmetrical dibenzalacetones containing substituents not regarded as "acid-forming" have been subjected to the action of phenylhydrazine and the products studied.

2. A hydrazone was obtained from styryl 4-dimethylaminostyryl ketone. In other cases rearrangement occurred so rapidly that the pyrazoline only could be isolated.

3. Oxidation of these products with permanganate gave, in the greater number of cases, the acids expected if the closing of the pyrazoline ring took place in the direction of the phenyl radical containing the "non-acidic" group. This is opposite that observed when ketones with "acid-forming" substituents were employed.

4. Further work is in progress.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Ozonolysis of Purely Aliphatic Olefins.[1] The Behavior of the Five Simplest Normal Alkyl Radicals in the Dehydration of Tertiary Alcohols

BY JAMES M. CHURCH WITH F. C. WHITMORE AND R. V. MCGREW

Although the first application of ozone to organic compounds was made in 1855[2] and in spite of the classical studies of Harries and his co-workers, detailed and specific directions for the *quantitative* isolation of the ozonolysis products of purely aliphatic olefins of low molecular weight are lacking. A surprisingly small amount of Harries' work dealt with such compounds.[3] The ozonolysis products of ethylene, propylene and butylene have been determined with precision.[4] Little exact work has been done on the methods of decomposing the ozonides. Among the methods used are treatment with zinc and acetic acid,[5] potassium ferrocyanide,[6] sodium bisulfite,[7] and catalytic hydrogenation.[8]

The present study of ozonolysis was undertaken to make available methods for the determination of mixtures of isomeric olefins as obtained by the dehydration of tertiary alcohols.[9]

In the present work the ozonides were prepared from solutions of the olefins in a mixture of paraffin hydrocarbons of boiling range 0–30°.[10] In some cases the ozonides were decomposed in the presence of the solvent. Usually, however, the low-boiling solvent was removed at low pressures, leaving the sirupy ozonides which were handled with proper precautions because of the danger of explosions. Most of the ozonides obtained in this work showed little explosibility. The ozonides of the highly branched and heavier olefins were most unstable to light and heat.

The best method for decomposing the ozonides was by treatment with water and zinc in the presence of traces of silver and hydroquinone.[1a] The catalysts[4] diminished the oxidation of the aldehydes by the hydrogen peroxide formed. This technique was adopted only after extensive studies of other methods of decomposing ozonides including those already mentioned and new meth-

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(1) *Cf.* Whitmore and Church (a) THIS JOURNAL, **54**, 3710 (1932); (b) *ibid.*, **55**, 1119 (1933).

(2) Schönbein, *J. prakt. Chem.*, **66**, 282 (1855).

(3) Harries and co-workers, *Ber.*, **37**, 845 (1904); **41**, 3098 (1908); **42**, 3305 (1909); *Ann.*, **343**, 311 (1905); **390**, 238 (1912).

(4) Briner and co-workers, *Helv. Chim. Acta*, **12**, 154, 181, 529 (1929); **14**, 794 (1931).

(5) (a) Harries and Haarmann, *Ber.*, **48**, 32, 231 (Witt) (1915); (b) Noller and Adams, THIS JOURNAL, **48**, 1074 (1926).

(6) Harries, *Chem. Zentr.*, IV, 292 (1920).

(7) Briner and Schnorf, *Helv. Chim. Acta*, **12**, 179 (1929).

(8) Fischer and co-workers, *Ann.*, **464**, 69 (1928); *Ber.*, **65**, 1468 (1932).

(9) *Cf.* Whitmore and Williams, THIS JOURNAL, **55**, 406 (1933).

(10) Supplied by the Viking Corporation of Charleston, W. Va.