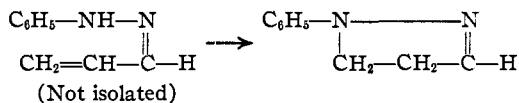


(CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA)

Rearrangement of the Phenylhydrazones of Some Unsymmetrically Substituted Dibenzalacetones¹

BY L. CHAS. RAIFORD AND JOHN B. ENTRIKIN

Phenylhydrazine and acrolëin² interact to give 1-phenylpyrazoline instead of the expected hydrazone. Later work² indicated that the



pyrazoline was formed through the rearrangement of a hydrazone, and that when the latter could be isolated, heating with acetic acid caused rearrangement. The stability of the phenylhydrazones of the type $\text{R—CH=CH—CO—R}'$ depends on the structures of both R and R'. When R is an aryl radical hydroxyl and alkoxy as substituents in it favor rearrangement, while the nitro radical tends to stabilize the hydrazone. Straus³ found that the hydrazones obtained from several symmetrically substituted dibenzalacetones rearranged easily when halogen is present in either ketone or hydrazine residue; if present in both, the hydrazone is stable.

Identification of Products.—The methods of distinguishing between these hydrazones and the pyrazolines include the following considerations. The tendency⁴ of the first to rearrange to the second is so pronounced that the Knorr⁵ color test for pyrazoline bases often shows the presence of the latter in the mother liquors from which the hydrazones were crystallized. Such solutions frequently show also a blue fluorescence if pyrazoline is present. When the product in question can be reduced by sodium amalgam⁶ to give aniline, it is regarded as a hydrazone.⁷ These are generally rearranged by boiling acetic acid.⁸ Products not reduced or rearranged are regarded as pyrazolines. To identify the latter directly Straus⁹ found that the product obtained by interaction of phenylhydrazine and dibenzal-

(1) From the thesis submitted in partial fulfilment of the requirements for the Ph.D. degree at the State University of Iowa.

(2) Auwers and collaborators, *Ber.*, **41**, 4230 (1908); **42**, 4412 (1909); **54**, 1000 (1921).

(3) Straus, *ibid.*, **51**, 1458 (1918).

(4) Auwers and Voss, *ibid.*, **42**, 4412, 4417 (1909).

(5) Knorr, *Ann.*, **238**, 200 (1887).

(6) Tafel, *Ber.*, **22**, 1854 (1889).

(7) Auwers and Kreuder [*ibid.*, **58**, 1983 (1925)] could not reduce the product, m. p. 120–121°, obtained from benzalacetone and *p*-tolylhydrazine. The compound was regarded as a hydrazone because boiling acetic acid changed it to an oil that gave a pronounced violet color when a sulfuric acid solution of it was treated with ferric chloride—a reaction given by pyrazolines generally.

(8) Auwers and Voss [*ibid.*, **42**, 4418 (1909)] failed to rearrange the product obtained from cinnamic aldehyde and *p*-nitrophenylhydrazine, although the compound was shown by reduction to be a hydrazone.

(9) Ref. 3, p. 1468.

acetone was oxidized by potassium permanganate to give 1,5-diphenylpyrazole-3-carboxylic acid¹⁰ and benzoic acid. He oxidized no product containing acidic substituents and none obtained from unsymmetrical ketones.

In the present work hydrazones were obtained from styryl 4-chlorophenyl and styryl 4-chlorostyryl ketones. In other cases pyrazolines only were isolated. Treatment of the hydrazones with sodium amalgam was unsatisfactory; repeated trials of the first one gave small quantities of aniline; the others gave none. They were rearranged by boiling with acetic acid. To decide which radical of the unsymmetrical ketone was involved in the formation of the pyrazoline and to determine the structure of the latter it was oxidized by the potassium permanganate.

Experimental Part

Styryl 4-Nitrostyryl Ketone.—To a solution of 20 g. of 4-nitrobenzaldehyde in 250 cc. of alcohol, somewhat above room temperature, 20 g. of benzalacetone were added with stirring and the mixture cooled to about 10°. Twenty cc. of 10% sodium hydroxide solution was then added, the stirring continued for two hours, the temperature kept below 18°, and the mixture allowed to stand overnight; yield, 40%. Crystallization from ethyl acetate gave brownish-yellow flakes; m. p. 178–179°.

Anal. Calcd. for $C_{17}H_{13}O_2N$: N, 5.02. Found: N, 4.75.

Other ketones required in this work are on record.

Phenylhydrazone of Styryl 4-Chlorophenyl Ketone.—To a solution of 20 g. of the required ketone¹¹ in 250 cc. of glacial acetic acid, 8.7 g. of phenylhydrazine was added with stirring, and the mixture allowed to stand for twenty-four hours; yield, 46%. Crystallization from alcohol gave yellow needles; m. p. 100–101°. ¹² Further crystallization gave a higher melting range, suggesting rearrangement. Boiling this material with acetic acid gave a product that melted at 149–150°, which was regarded as a pyrazoline. The same product was obtained when the original reaction mixture was allowed to stand for five days at room temperature.

*Anal.*¹³ Calcd. for $C_{21}H_{17}N_2Cl$: Cl, 10.67. Found: Cl, 10.36.

The phenylhydrazone of styryl 4-chlorostyryl ketone was obtained in yellow needles that melted at 165–166°; yield, 60%. Recrystallization from acetic acid, acetone, alcohol or ethyl acetate caused partial rearrangement. Boiling it for an hour with acetic acid rearranged it completely to the pyrazoline; m. p. 184–185°.

Anal. Calcd. for $C_{23}H_{19}N_2Cl$: Cl, 9.90. Found: Cl, 10.33.

Oxidation of Pyrazolines.—In general, 10 g. of pyrazoline was suspended in 200 cc. of water containing 5 g. of sodium carbonate, and this mixture was boiled under a reflux condenser while 40–45 g. of solid permanganate was added in 3 to 4 g. portions as long as the purple color was discharged, usually several hours. The mixture was filtered, the residue digested with sodium hydroxide solution and filtered, and the combined filtrates acidified. The acids liberated were collected and subjected to steam distillation to remove benzoic acid. The non-volatile pyrazole acid was then purified.

(10) Beyer and Claisen, *Ber.*, **20**, 2186 (1887).

(11) The product used here, made by a standard method, melted at 97°. Dilthey [*J. prakt. Chem.*, **101**, 199 (1920)] recorded 101°.

(12) Repeated attempts to reduce this material by sodium amalgam gave small quantities of aniline.

(13) Brown and Beal, *This Journal*, **45**, 1291 (1923).

Compounds 2, 3, 4 and 5 (see table) gave small¹⁴ yields of 1,5-diphenylpyrazole-3-carboxylic acid. In all cases except that containing the 3-nitrostyryl radical the required substituted benzoic acid was also isolated in small yield.¹⁵ Table I gives the composition and other properties of the pyrazolines.

TABLE I
PYRAZOLINES FROM UNSYMMETRICAL α,β -UNSATURATED KETONES

Substituted aryl radicals, 1,5-diphenyl-3-		Solvent	Crystal form	
(1)	(4-Chlorophenyl)-	Alcohol	Yellow needles	
(2)	(3-Chlorostyryl)-	Ethyl acetate	Dark yellow needles	
(3)	(4-Chlorostyryl)-	Ethyl acetate	Deep yellow needles	
(4)	(3-Nitrostyryl)-	Acetic acid	Orange needles	
(5)	(4-Nitrostyryl)-	Alcohol ^b	Red nodules	

Formula	M. p., °C.	Analyses			
		Halogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found
C ₂₁ H ₁₇ N ₂ Cl	149-150	10.67	10.71
C ₂₂ H ₁₈ N ₂ Cl	153-154	9.90	9.94
C ₂₂ H ₁₉ N ₂ Cl	184-185	9.90	10.16
C ₂₃ H ₁₉ O ₂ N ₃	182-183	11.38	11.01 ^a
C ₂₃ H ₁₉ O ₂ N ₃	191-192	11.38	11.30

^a Done by a modification of Kürschner's method [*Z. anal. Chem.*, **68**, 209 (1926)].

^b Crystallization from acetic acid gave irregularly shaped crystals that appeared to decompose with frothing at 130-131°. and gave a clear liquid at about 190°, which suggested solvent of crystallization. When heated for twenty-four hours at 135°, 1.9377 g. lost 0.2529 g. Calcd. for C₂₃H₁₉O₂N₃·C₂H₄O₂: C₂H₄O₂, 13.99. Found: C₂H₄O₂, 13.05. Separate portions of the original material and of the residue left after removal of acetic acid of crystallization, respectively, were crystallized from alcohol. In each case small red crystals that melted at 191-192° were obtained.

Summary and Conclusions

1. Several unsymmetrically substituted dibenzalacetones have been condensed with phenylhydrazine. Hydrazones were isolated in some cases, and in others the products rearranged immediately to the isomeric pyrazolines.

2. In the rearrangement of these hydrazones the closing of the pyrazoline ring involved the unsaturation farthest away from the phenyl nucleus containing the halogen or nitro radical. This was indicated by the fact that in the oxidation of the pyrazolines 1,5-diphenylpyrazole-3-carboxylic acid and benzoic or a substituted benzoic acid were obtained.

(14) Doubtless due to further oxidation of the pyrazole acid. Oxidation of 1,5-diphenyl-3-styryl-pyrazoline, by G. V. Gundy of this Laboratory, gave 39% of the pyrazole acid and 137% of the required benzoic acid. Treatment of a purified sample of pyrazole acid with permanganate gave benzoic acid.

(15) Zimmerman (unpublished work) treated pure bromo- and nitrobenzoic acids with alkaline permanganate and noted destruction of the acids to the extent of 20% or more. When the ketones here used were condensed with *p*-nitro- and *p*-bromophenylhydrazines the initial products had melting points and other properties different from those shown by the compounds obtained by boiling the initial ones with acetic acid. The first were probably hydrazones and the final ones pyrazolines. Oxidation of the latter with permanganate seemed to cause complete degradation. From the product obtained by interaction of 4-bromophenylhydrazine with styryl 3-nitrostyryl ketone, only a small amount of benzoic acid was isolated. The bromide ion was easily detected in the reaction mixture.

3. Oxidation of pyrazolines containing a bromine atom or a nitro radical in the hydrazine residue seemed to cause complete degradation of the molecule. These compounds are still being studied.

IOWA CITY, IOWA

RECEIVED AUGUST 26, 1932
PUBLISHED MARCH 7, 1933

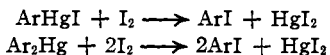
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY AND OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Interconversion of Arylmercuric Halides and Diarylmercury Compounds. I

BY FRANK C. WHITMORE AND R. J. SOBATZKI¹

The reaction, $\text{Ar}_2\text{Hg} + \text{HgX}_2 \rightleftharpoons 2\text{ArHgX}$, has been the subject of many studies.²

The present investigation deals with the influence of inorganic iodides on the reaction. It was suggested by the observation that while sodium iodide in alcoholic solution reverses the reaction in the case of para tolyl compounds, giving a complete conversion to di-*p*-tolylmercury, it has no effect on phenylmercuric iodide. Early in the investigation cases were found in which the reversibility of the reaction by sodium iodide lay between these extremes. Consequently it became necessary to develop a method for analyzing mixtures of Ar_2Hg and ArHgI . This was accomplished satisfactorily by iodimetry.³ The method can best be illustrated by the two equations



Thus a given amount of mercury in a diarylmercury will react with twice as much iodine as the same amount of mercury in an arylmercuric iodide. The method was found to give satisfactory results with known mixtures of arylmercuric halides and diarylmercury compounds.

The following arylmercuric iodides were converted to the mercury diaryls by refluxing with an excess of alcoholic sodium iodide: *o*-tolyl, *m*-tolyl, *p*-tolyl, *m*-xylyl, mesitylyl, α -naphthyl and β -naphthyl. Phenylmercuric iodide showed no change even after refluxing for three hundred hours with alcoholic sodium iodide. Benzyl- and cyclohexylmercuric iodides decomposed on long heating with sodium iodide. *p*-Ethylphenyl-

(1) Research Fellow of the Public Health Institute of Chicago. This paper is abstracted from a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree at Northwestern University.

(2) Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, 1921, pp. 59-67; Whitmore, THIS JOURNAL, **41**, 1841 (1919); Hein and Wagler, *Ber.*, **58B**, 1499 (1925); Jurgens, *Rec. trav. chim.*, **45**, 61 (1926); Whitmore, Hanson and Carnahan, THIS JOURNAL, **51**, 894 (1929).

(3) This method was developed at Northwestern University by Messrs. Louis Ehrenfeld and R. J. Sobatzki independently, the former for analyzing mixtures of C-Hg and O-Hg compounds and the latter for analyzing mixtures of C-Hg and C-Hg-C compounds.