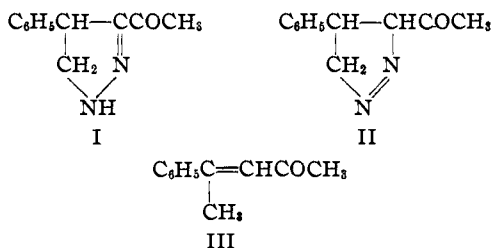


[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Action of Aliphatic Diazo Compounds upon α,β -Unsaturated Ketones. III.¹ Benzalacetone and Diazomethane

BY LEE IRVIN SMITH AND KENNETH L. HOWARD

Azzarello² investigated the addition of diazomethane to benzalacetone and dibenzalacetone.³ The product obtained from benzalacetone was Δ^2 -3-aceto-4-phenylpyrazoline (I) which was char-



acterized by a series of color reactions, by formation of several metallic derivatives, by its oxime, by oxidation to the known 3-carboxy-4-phenylpyrazole, and by thermal decomposition, although the decomposition products were not identified. It appeared curious to us that the usual first product of the reaction, the Δ^1 -pyrazoline (II), was not obtained from benzalacetone; moreover, pyrolysis of either of these pyrazolines would be expected to lead to substances which could be readily isolated and identified. We therefore repeated the work of Azzarello upon the addition of diazomethane to benzalacetone.

Diazomethane in ether solution readily added to benzalacetone to give almost quantitative yields of the known Δ^2 -pyrazoline, I, m. p. 101°. In one experiment only was there any indication of the formation of the isomeric Δ^1 -pyrazoline; in this case, the white product melted at 90–92°, immediately solidified, and then melted at 99°. Attempts to repeat this experiment under a variety of conditions were unsuccessful, and it appears that this Δ^1 -pyrazoline rearranges so readily into the Δ^2 -isomer that once the laboratory bench and glassware have been in contact with the stable isomer, no other product can be obtained. A similar difficulty, though not nearly so marked, was observed in the case of the dibenzoylpyrazolines previously studied.¹ After repeated crystallizations, the Δ^2 -pyrazoline (I)

melted at 101°, and not at 105–106° as reported by Azzarello. The oxime of I melted at 181°, in agreement with Azzarello's report of 181–182°.

Pyrolysis of I at 230–245° at atmospheric pressure for thirty minutes produced, in poor yield, a yellow oil which boiled at 135–136° under 18–19 mm. When the pyrolysis was carried out under reduced pressure, much better results were obtained, and at 190–205° under 16–20 mm. the products distilled from the reaction mixture as fast as they were formed. The chief product, formed in 40% yield, was a light yellow oil $\text{C}_{11}\text{H}_{12}\text{O}$ which boiled at 130–131° under 14–15 mm. and which darkened rapidly in the air. The substance was a ketone, for it formed a semicarbazone, m. p. 183.5–184°. When the ketone was ozonized in chloroform solution, it gave acetophenone, which was identified via the semicarbazone and phenylhydrazone; the original ketone, therefore, was identified as β -methylbenzalacetone, III.

Addition of diazomethane to benzalacetone, therefore, follows the usual course in giving a pyrazoline in which the methylene group of the diazo compound is attached to the β -carbon atom of the ketone. Pyrolysis of this pyrazoline likewise follows one of the usual courses taken by such reactions; in this case, the product is the β -alkyl (methyl) derivative of the original unsaturated ketone. No cyclopropane derivative was isolated.

Experimental Part⁴

3-Aceto-4-phenylpyrazoline (I).—A solution of diazomethane (5.3 g., 0.126 mole) in ether (150 cc.) was dried over solid potassium hydroxide at -14° for two hours and then decanted into a cold (-14°) solution of benzalacetone (22 g., 0.150 mole) in dry ether (100 cc.). After the solution had stood at $-5-0^\circ$ for one and one-quarter hours, the white solid (I) was filtered and the ether was evaporated from the filtrate. The residue weighed 10.1 g. and was benzalacetone. The white pyrazoline I weighed 15.0 g. (98.8% based upon the ketone consumed) and melted at 100.5–101°. When recrystallized from aqueous methanol (1:2) the substance formed pale yellow crystals which melted at 101°, and further crystallization did not give a product with a higher melting point. Attempts to convert this substance into an isomer were unsuccessful.

(1) Paper II, THIS JOURNAL, 65, 159 (1943).

(2) Azzarello, *Gazz. chim. ital.*, 36, 11, 50 (1906).

(3) Smith and Pings, *J. Org. Chem.*, 2, 23 (1937). The statement on page 24 of this paper is in error. Azzarello's work was overlooked at the time.

(4) Microanalyses by C. H. Stratton and E. E. Renfrew.

When it was heated at 110–115° for thirty minutes, no changes resulted and the melting point was the same. The substance, therefore, is the Δ^2 -pyrazoline. In an experiment duplicating the one above, except that the temperature was maintained at –14 to –15° throughout, a small amount of white crystals suddenly formed after the solution had stood for forty-five minutes. No apparent increase in the amount of solid was observed after two hours; the solid (about 0.1 g.) was then removed from the ethereal solution. This white solid melted at 90–92°, and immediately resolidified to a yellow material which then melted at 98–100°. The main part of the reaction product, isolated later, was crystallized from methanol. It was white and melted at 100.5–101°. Complete removal of the solvent under reduced pressure caused a part of the material to be transformed into the yellow form. The white and yellow crystals were separated mechanically; both melted at 100.5–101°. The material in the melting point tube always solidified to a yellow crystalline solid, regardless of whether the initial material was white or yellow. Rapid or slow melting of the white solid did not change the melting point, and the transformation which occurred at 90–92° was never observed again.

Oxime.—This was prepared in the usual way; after one crystallization from aqueous ethanol it melted at 181° in agreement with Azzarello's report of 181–182°.

Pyrolysis of I.—The pyrazoline I (6.75 g.) was heated at 190–205° under 16–20 mm. for two hours in an apparatus arranged for distillation. The distillate, consisting of an oil and some solid (I), was transferred to a Claisen flask and distilled under reduced pressure in an atmosphere of nitrogen. The fraction boiling at 132–138° under 17 mm. (2.77 g., 46%) had n_D^{20} 1.5662 and was β -methylacetophenone. The ketone decolorized a solution of potassium permanganate in acetone and it readily added bromine.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.50; H, 7.50. Found: C, 81.96; H, 7.40.

Under atmospheric pressure, decomposition of the pyrazoline began at 135°, and was very rapid at 230–235°.

After thirty minutes at this temperature, the material yielded only 7.5% of the ketone.

Semicarbazone.—This was prepared in the usual way and recrystallized three times from aqueous ethanol. It then melted at 183.5–184°.

Anal. Calcd. for $C_{12}H_{15}ON_3$: C, 66.36; H, 6.91. Found: C, 66.21; H, 6.87.

Ozonolysis.—A stream of ozonized oxygen was passed for ten minutes through a cooled solution of β -methylbenzalacetone (0.618 g., 0.0037 mole) in chloroform (22 cc.). The solvent was removed from the colorless solution under reduced pressure at room temperature, and the residual ozonide was reductively cleaved by boiling it for forty-five minutes with water (50 cc.), zinc (3 g.), a small crystal each of silver nitrate and hydroquinone.⁵ The mixture was steam distilled and the distillate was extracted with ether. Evaporation of the ether left a residue of light colored oil (3 or 4 drops) which was identified as acetophenone by preparation of the phenylhydrazone (m. p. 97–98°) and the semicarbazone (m. p. 194.5–195°) and comparison of these with authentic specimens.

Summary

1. The product obtained by the reaction of benzalacetone and diazomethane is Δ^2 -3-aceto-4-phenylpyrazoline, and Azzarello's work has been confirmed. Evidence was obtained that the Δ^1 -pyrazoline, is actually formed first, but that it is extremely labile and changes rapidly into the Δ^2 -isomer.

2. This pyrazoline was pyrolyzed and β -methylbenzalacetone was identified as the chief product of the decomposition. No cyclopropane derivative was isolated.

(5) Whitmore and Church, *THIS JOURNAL*, **54**, 3710 (1932); Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MARYLAND]

The Rate of Conversion of Ammonium Cyanate to Urea in Non-aqueous Solvents. VI¹

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The rate of conversion of ammonium cyanate to urea in five non-aqueous solvents over a 30° temperature range is reported in this research. The previous papers⁴ of this series were con-

cerned with studying the reaction in various solvent-water mixtures over a 30° temperature range and at various constant dielectric constants. It was considered worth while to study the reaction in one-component solvents at varying dielectric constant. The reaction was carried out in methanol, ethanol, isopropanol, ethylene glycol and glycerol. Calculations based on the experimental data are compared with those obtained from existing solution kinetic theories.

(1) Presented at the Buffalo meeting of the A. C. S., September, 1942.

(2) Part of a thesis submitted by Selmer Peterson to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Present address: Mellon Institute of Industrial Research, Pittsburgh, Pa.

(4) Svirbely and Lander, *THIS JOURNAL*, **61**, 3538 (1939), was the last paper of the series.