2,4-Dinitrophenylhydrazones. V. The Formation of 1-(2,4-Dinitrophenyl)pyrazolines from Methylol Ketones[1,2]

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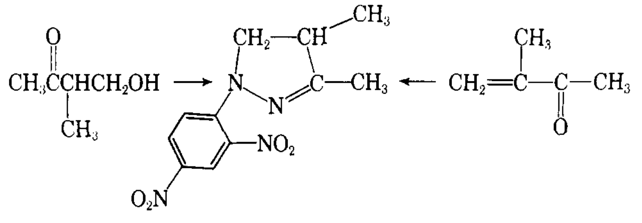
It is found that the reaction of 2,4-dinitrophenylhydrazine with 3-methyl-4-hydroxybutanone and 3-hydroxymethyl-4-heptanone gives the 2,4-dinitrophenylhydrazones of the dehydrated ketones rather than the isomeric 2,4-dinitrophenylpyrazolines. The authentic pyrazolines and 3-(2-methyl-3-oxobutyl)-6-nitrobenzotriazole 1-oxide are reported. It appears that, in contrast to general belief, the reaction of methylol ketones with 2,4-dinitrophenylhydrazine does not lead to 1-(2,4-dinitrophenyl)-2-pyrazolines.

Until n.m.r. spectroscopy became available as an analytical tool it was not easy to distinguish unsaturated 2,4-dinitrophenylhydrazones from the isomeric 1-(2,4-dinitrophenyl)-2-pyrazolines. Although it is thought that the reaction of 2,4-dinitrophenylhydrazine with an α,β-unsaturated carbonyl compound gives the 2,4-dinitrophenylhydrazone rather than the pyrazoline, reaction with some types of β-substituted carbonyl compounds is regarded as a method of synthesizing the corresponding pyrazolines.[3] Among these are β-hydroxy ketones. In the previous paper[4] it was shown that the reaction of some β-alkoxy ketones with 2,4-dinitrophenylhydrazine resulted in the formation of some new compounds, the 3-(3-oxoalkyl)-6-nitrobenzotriazole 1-oxides. We were able to distinguish among the isomeric 2,4-dinitrophenylhydrazones, pyrazolines, and benzotriazole oxides by absorption and n.m.r. spectroscopy. It also was found that 4-hydroxybutanone reacted similarly to give 3-(3-oxobutyl)-6-nitrobenzotriazole 1-oxide. It was noted that this result contrasted with reports that the reaction of β-hydroxy ketones with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylpyrazolines.[5-8] In order to clarify this phase of pyrazoline chemistry we have re-examined some of the cases in the literature and find that the products reported appear to be not the pyrazolines but the unsaturated 2,4-dinitrophenylhydrazones and, in one case, the isomeric benzotriazole oxide.

Results and Discussion

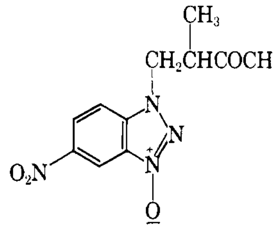
3-Methyl-4-hydroxybutanone.—It is reported[5] that the boiling of this ketone for several hours with 2,4-dinitrophenylhydrazine in an acidic ethyl alcohol solution gave 1-(2,4-dinitrophenyl)-3,4-dimethylpyrazoline (I). Similar treatment of methyl isopropenyl ketone also gave I.



I

The melting point of the product was 191°. We have repeated these experiments. Preparation of the 2,4-dinitrophenylhydrazone of methyl isopropenyl ketone by the diglyme method[9] for α,β-unsaturated ketones gave the red derivative, m.p. 192.7–193.7°, $\lambda_{\max}^{\text{EtOH}}$ 369 mμ. An identical product was obtained by treating the methylol ketone as described.[5] Authentic I was made from 3,4-dimethylpyrazoline by the method of Chambers and Willard.[10] The product had m.p. 108.5–110.5°, $\lambda_{\max}^{\text{EtOH}}$ 392 mμ. The 2,4-dinitrophenylhydrazone of methyl isopropenyl ketone is reported by Martin[11] as having m.p. 190°, $\lambda_{\max}^{\text{EtOH}}$ 371 mμ. The ultraviolet absorption maximum for authentic I is consistent with 391 mμ for the 3-methyl- and 394 mμ for the 3-ethyl-1-(2,4-dinitrophenyl)pyrazolines described in our last paper.[4]

Because we had found that 4-hydroxybutanone in similar circumstances gave a ketoalkyl benzotriazole oxide we were interested in preparing the analogous compound in the present case. This was achieved by the reaction of 6-nitrobenzotriazole oxide with methyl isopropenyl ketone. The product (II) had m.p. 181.3–181.8°, $\lambda_{\max}^{\text{EtOH}}$ 263 and 349 mμ, and showed a strong carbonyl absorption at 1730 cm.$^{-1}$.



II

It also is reported elsewhere[6] that the reaction of 3-methyl-4-hydroxybutanone with 2,4-dinitrophenylhydrazine gives the pyrazoline (I), but the melting point is given as 180–181.5°. It appears that the product may have been II rather than the pyrazoline.

We report also the 2,4-dinitrophenylhydrazone of the 3-methyl-4-hydroxybutanone, prepared by the diglyme method[9] and having the m.p. 107–109°, $\lambda_{\max}^{\text{EtOH}}$ 361 mμ.

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[1] Taken from the M. S. degree thesis of Miss Julie Y.-F. Tsai, Texas Technological College, August, 1963.

[2] This work was supported by Grant No. 1603-AD(2) and by the Institute of Science and Engineering, Texas Technological College.

[3] T. L. Jacobs, "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 64–68.

[4] H. J. Shine, L.-T. Fang, H. E. Mallory, N. F. Chamberlain, and F. Stehling, *J. Org. Chem.*, **28**, 2326 (1963).

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[7] R. L. Wear, *J. Am. Chem. Soc.*, **73**, 2390 (1951).

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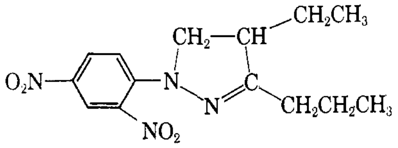
3-Hydroxymethyl-4-heptanone.—The product of reaction of this ketone with 2,4-dinitrophenylhydrazine is described[7] as 1-(2,4-dinitrophenyl)-3-propyl-4-ethylpyrazoline (III), m.p. 118–119.5°. This is actually the



III

2,4-dinitrophenylhydrazone of 2-ethyl-1-hexen-3-one, m.p. 119.5–120.5°, $\lambda_{\max}^{\mathrm{EtOH}}$ 370 mμ, which we have made from the methylol ketone and directly by the diglyme method from the unsaturated ketone.

The authentic III was made and has m.p. 73.7–76.2°, $\lambda_{\max}^{\mathrm{EtOH}}$ 393 mμ.

We were unable to prepare the corresponding 6-nitrobenzotriazole oxide or the 2,4-dinitrophenylhydrazone of the methylol ketone.

Thus, it is found in these examples that the reaction of 2,4-dinitrophenylhydrazine with β-hydroxy ketones does not lead to the pyrazolines. By analogy, it seems probable that the three pyrazolines reported by Spriggs, Hill, and Senter[8] are the 2,4-dinitrophenylhydrazones of the corresponding unsaturated ketones. These examples[8] were not reinvestigated by us.

Experimental[12]

Reaction with 3-Methyl-4-hydroxybutanone.—This compound was prepared as described by Morgan and Holmes,[5] and had b.p. 82–87° (11 mm.), $n^{20}\mathrm{D}$ 1.4319. The 2,4-dinitrophenylhydrazone was prepared in diglyme[9] and recrystallized from methanol, m.p. 107–109°.

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: C, 46.81; H, 5.00; N, 19.85. Found: C, 47.01; H, 5.12; N, 19.66.

Three grams of the ketone was boiled for 6 hr. (to complete solution) with 3 g. of 2,4-dinitrophenylhydrazine and 0.5 ml. of concentrated hydrochloric acid in 20 ml. of ethyl alcohol. The red precipitate which formed on cooling was recrystallized from ethyl acetate and had m.p. 195.5–196°. The infrared spectrum (potassium bromide pellet) was identical with that of the 2,4-dinitrophenylhydrazone of methyl isopropenyl ketone.

Methyl isopropenyl ketone was prepared from the commercially available dimer (Chemical Intermediates and Research Laboratories, Cuyahoga Falls, Ohio). After fractional distillation, the product had b.p. 89–92° (680 mm.), $n^{20}\mathrm{D}$ 1.4230; lit.[11] b.p. 98° (760 mm.), $n^{20}\mathrm{D}$ 1.4232. The 2,4-dinitrophenylhydrazone had m.p. 192.7–193.7° (ethyl acetate); lit.[11] m.p. 190°.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 49.95; H, 4.52; N, 20.81.

3-(2-Methyl-3-oxobutyl)-6-nitrobenzotriazole 1-Oxide (II).—A solution containing 0.5 g. of methyl isopropenyl ketone and 5 drops of concentrated hydrochloric acid was shaken overnight with 0.5 g. of 6-nitrobenzotriazole 1-oxide. Bright yellow crystals had formed and most of the 6-nitrobenzotriazole oxide had disappeared. The filtered solids were washed with hot water, and the residue was crystallized from hot ethyl alcohol–acetone. Yellow needles, m.p. 181.3–181.8°, formed. The infrared spectrum (potassium bromide pellet) was very similar to the spectra of the oxobutyl and oxopentyl analogs.[4]

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 49.69; H, 4.56; N, 21.40.

1-(2,4-Dinitrophenyl)-3,4-dimethylpyrazoline (I).—Methyl isopropenyl ketone and hydrazine hydrate were used to prepare 3,4-dimethylpyrazoline. The method of Beech, Turnbull, and Wilson[13] was used. The preparation was carried out under nitrogen, and the product was distilled under nitrogen. The crude product, b.p. 40–60° (3 mm.), was used for reaction in ether with 1-bromo-2,4-dinitrobenzene as described by Chambers and Willard.[10] The yellow product was crystallized from ether–petroleum ether (b.p. 30–60°) and had m.p. 108.5–110.5°.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 49.91; H, 4.55; N, 20.94.

Reactions with 3-Hydroxymethyl-4-heptanone.—This compound was prepared from ethyl ketene dimer as described by Wear.[7] The product had b.p. 94–99° (5 mm.), $n^{20}\mathrm{D}$ 1.4426; lit.[7] b.p. 75° (1.5 mm.), $n^{23}\mathrm{D}$ 1.4389.

Three grams of the ketone, 4 g. of 2,4-dinitrophenylhydrazine, and 0.5 ml. of concentrated hydrochloric acid were boiled for 3 hr. The red precipitate obtained on cooling was crystallized from ethyl alcohol–ethyl acetate, petroleum ether–ethyl acetate, and finally ethyl alcohol, to give red needles, m.p. 120.5–121°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92; N, 18.29. Found: C, 55.03; H, 6.09; N, 18.53.

Treating the methylol ketone with 2,4-dinitrophenylhydrazine by a standard method for making 2,4-dinitrophenylhydrazones[14] gave red needles (ethyl alcohol), m.p. 120.5–121°. This had an infrared spectrum (potassium bromide pellet) identical with the product, m.p. 120.5–121°, reported above and with the 2,4-dinitrophenylhydrazone of the unsaturated ketone, below.

2-Ethyl-1-hepten-3-one.—This was prepared in poor yield by the *p*-toluenesulfonic acid-catalyzed dehydration of the methylol ketone. The product had b.p. 95° (95 mm.), $n^{20}\mathrm{D}$ 1.4356. A better yield of the ketone was obtained by the longer chloromethylation and dehydrohalogenation procedure described by Colonge.[15] The product had b.p. 70–74° (40 mm.), $n^{20}\mathrm{D}$ 1.4344; lit.[15] b.p. 157–159° (742 mm.), $n^{18}\mathrm{D}$ 1.4408.

The 2,4-dinitrophenylhydrazone, prepared in diglyme,[9] had m.p. 119.5–120.5°.

An attempt to convert the unsaturated ketone to the substituted 6-nitrobenzotriazole oxide by reaction with 6-nitrobenzotriazole 1-oxide in acidic ethyl alcohol was unsuccessful.

1-(2,4-Dinitrophenyl)-3-propyl-4-ethylpyrazoline.—The 2-ethyl-1-hexen-3-one was converted to 3-propyl-4-ethylpyrazoline by the standard method.[13] The crude product, b.p. 86–91° (7 mm.), was used directly to prepare the 1-(2,4-dinitrophenyl)-pyrazoline.[10] The product was an oily solid which was recrystallized only with difficulty several times from petroleum ether and finally from *n*-hexane to give a product with m.p. 73.7–76.2°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92; N, 18.29. Found: C, 54.66; H, 6.24; N, 18.03.

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[12] Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

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