[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

A NEW METHOD OF PREPARING 2,4-DINITROPHENYLHYDRAZONES WHICH FURNISHES PROOF OF THE MOLECULAR STRUCTURE OF THESE COMPOUNDS AND MAY BE USED IN THE QUALITATIVE IDENTIFICATION OF UNSUBSTITUTED HYDRAZONES[1]

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The 2,4-dinitrophenylhydrazones of high molecular weight aliphatic ketones such as methyl *n*-octyl ketone, di-*n*-butyl ketone, di-*n*-amyl ketone, di-*n*-nonyl ketone, di-*n*-undecyl ketone, di-*n*-pentadecyl ketone, and di-*n*-heptadecyl ketone appear either to form as oils or not to form at all (1, 2, 3). This could be due to one of two possible causes: (a) the 2,4-dinitrophenylhydrazones form low-melting eutectic mixtures or solid solutions with components of or impurities in the reaction mixture (4, 5); (b) the size of the side chains of the ketone could sterically block the large aromatic nucleus in its attack on the carbonyl group (3). In support of the latter statement, the oximes of these same ketones do form, but with difficulty.

If the trouble is due solely to the existence of impurities, then a new reaction procedure involving different reagents might be of value. If, on the other hand, a steric effect is involved, a new reaction method consisting of the insertion of the aromatic nucleus after the azomethine bond had been formed might be successful. For these reasons we decided to try to form the 2,4-dinitrophenylhydrazones by reacting the unsubstituted hydrazone with 2,4-dinitrochlorobenzene.

The 2,4-dinitrophenylhydrazones of acetone and methyl *n*-hexyl ketone were prepared in this manner and were identified by comparison of their physical properties with those of the derivatives made in the usual manner (6). The 2,4-dinitrophenylhydrazone of di-*n*-butyl ketone was prepared for the first time in a similar manner (m.p. 40.5–41.0°). The method is applicable to any unsubstituted hydrazone.

Besides pointing the way to the synthesis of the 2,4-dinitrophenylhydrazones of the high molecular weight aliphatic ketones, the reaction has served to illustrate, by chemical means, that the 2,4-dinitrophenylhydrazones have the same molecular type structure as the unsubstituted hydrazones. In addition, it may be used as a qualitative method of identifying unsubstituted hydrazones by converting them to the corresponding 2,4-dinitrophenylhydrazones.

EXPERIMENTAL

Carbonyl compounds, A commercial grade of *acetone* was fractionated before use. The *methyl n-hexyl ketone* was prepared by the sodium dichromate oxidation of capryl alcohol

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(7) and distilled, b.p. 170–171°/733 mm. The *di-n-butyl ketone* was used as purchased from Eastman Kodak Co.

Acetone hydrazone. The hydrazone of acetone was prepared essentially by the procedure of Curtius and Pflug (8), b.p. 122–126°/729 mm., yield, 31%.

Methyl n-hexyl ketone hydrazone. This compound was prepared in a manner similar to the above one. A 4 g. (0.08 mole) sample of 100% hydrazine hydrate was placed in a 100 cc. round-bottom flask. In order to have a homogeneous medium upon the addition of the ketone, 5 cc. of 95% ethyl alcohol was introduced. To this mixture was added, over a period of a half-hour and with agitation, 10.0 g. (0.078 mole) of methyl *n*-hexyl ketone and 15.3 g. (0.1 mole) of solid barium oxide. When the addition was complete, the reaction mixture was refluxed on a steam-bath for five hours, cooled, and extracted with both warm and cold 95% ethyl alcohol. The solid residue was washed with cold alcohol, and the washings added to the other extracts. The total volume at this point was about 75 cc. The liquid extract was distilled at 736 mm. The material boiling from 217–225° was collected. The yield was 58% (6.5 g.).

Di-n-butyl ketone hydrazone. In a 100 cc. boiling flask was placed 8.24 (0.16 mole) of 100% hydrazine hydrate. A little solid barium oxide was added to this, and then 10.0 g. (0.007 mole) of di-*n*-butyl ketone was added slowly with shaking over a half-hour period. From time to time more solid barium oxide was added until 25.0 g. in all had been used. About 100 cc. of absolute ethyl alcohol was required to keep a homogeneous reaction mixture. The reaction was slow in starting as shown by the absence of any noticeable heat evolution. It was started by warming gently on a steam-bath for a few minutes. When everything had been added, the reaction mixture was allowed to cool to a solid mass. It was then refluxed on a steam-bath for 14 hours. When cool, the mass was ether-extracted. The extract was distilled and the hydrazone was collected, b.p. 225–228°/735 mm. The yield was 38.2% (5.0 g.).

Preparation of the 2,4-dinitrophenylhydrazones. The various 2,4-dinitrophenylhydrazones were prepared from the unsubstituted hydrazones and 2,4-dinitrochlorobenzene by a modification of Allen's preparation of 2,4-dinitrophenylhydrazine itself (9). The details for the preparing of the acetone derivative will be sufficient to illustrate the general procedure.

To 1.5 g. (0.020 mole) of acetone hydrazone dissolved in 10 cc. of 95% ethyl alcohol was added a solution of 4.0 g. (0.019 mole) of 2,4-dinitrochlorobenzene in 30 cc. of 95% ethyl alcohol. The mixture was refluxed for about an hour, cooled, and filtered. The residue was washed with warm alcohol to remove any 2,4-dinitrochlorobenzene and the precipitate was allowed to dry. It was recrystallized once from 95% ethyl alcohol, m.p. 123°.

The 2,4-dinitrophenylhydrazones of acetone and methyl *n*-hexyl ketone were identified by comparing their optical crystallographic properties to those of the derivatives prepared by the usual procedure outlined in Shriner and Fuson (6).

The 2,4-dinitrophenylhydrazone of di-*n*-butyl ketone was prepared from the unsubstituted hydrazone in the above manner. A red oil formed at first, but it solidified after a few days. The compound was recrystallized to the constant m.p. of 40.5–41.0° from both 95% ethyl alcohol and ligroin.

Anal. Calc'd: N, 17.38. Found: N (Dumas), 17.30.

SUMMARY

1. A new method for preparing the 2,4-dinitrophenylhydrazones by reacting the unsubstituted hydrazone with 2,4-dinitrochlorobenzene was reported. The 2,4-dinitrophenylhydrazone of di-*n*-butyl ketone was prepared in this way for the first time, m.p. 40.5–41.0°.

2. The reaction illustrates the similarity in the structures of the unsubstituted hydrazones and the 2,4-dinitrophenylhydrazones, establishing the presence of the azomethine bond in the latter compounds.

3. The reaction may be used as a qualitative method of identifying unsub-

stituted hydrazones by converting them to their corresponding 2,4-dinitrophenylhydrazones.

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