[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

THE IDENTIFICATION OF CARBONYL COMPOUNDS BY USE OF 2,4-DINITROPHENYLHYDRAZINE

BY CHARLES F. H. ALLEN

RECEIVED MARCH 20, 1930 PUBLISHED JULY 3, 19 0

In connection with another investigation under way in this Laboratory, use of the common reagents for a carbonyl group failed to give a solid derivative. At about the same time it was noted that there was no reliable rapid reagent for preparing solid derivatives of most of the aliphatic aldehydes and ketones. As a rule the reagents that form crystalline products with aromatic carbonyl compounds give oils with most of the corresponding aliphatic substances; in spite of this, Laboratory manuals in illustrating the preparation of characteristic derivatives, usually select their examples from the aromatic series.[1] Consequently when a decomposition product obtained in a research is an aliphatic carbonyl compound, as is frequently the case, the average student is at a loss as to a reliable method of identification. As a remedy, the use of substituted phenylhydrazines is often recommended; they have the disadvantages of a high cost or difficulty of preparation. After trying out several, we finally selected 2,4-dinitrophenylhydrazine as the one best meeting the above objections.

It can be prepared easily in the laboratory from inexpensive reagents by persons with slight experience. It gives good crystalline derivatives with most of the common aliphatic carbonyl compounds; if necessary, these solids are readily purified by recrystallization from alcohol. It can be used in the presence of water (*i. e.*, dilute solutions) in many instances.[2]

It seems strange that such a useful reagent is not more widely known. Probably this is because it was applied by its discoverers almost entirely to aromatic compounds,[3,4] which form crystalline products with phenylhydrazine itself, hence offered no particular advantage. Brady and Elsmire[5] call attention to its use with a few aliphatic aldehydes and one ketone, but their paper does not seem to have received the attention it deserves.

We have attempted to determine roughly the limits of its usefulness by applying it to all available carbonyl compounds. The results are shown

---

[1] Adams and Johnson, "Elementary Laboratory Experiments in Organic Chemistry," The Macmillan Co., New York, **1928**. Norris, "Experimental Organic Chemistry," McGraw-Hill Book Co., Inc., New York, **1924**, 2d ed., p. 163; Cohen, "Practical Organic Chemistry," Macmillan and Co., Ltd., London, **1928**; Noyes, "Organic Chemistry," Chemical Publishing Co., Easton, Pa., 4th ed., revised, **1920**; Thorpe and Whiteley, "Student's Manual of Organic Chemical Analysis," Longmans, Greene and Co., Ltd., London, **1926**.

[2] Kahlenberg, *Science*, **61**, 344 (1925).

[3] Purgotti, *Gazz. chim. ital.*, **24**, I, 555 (1894).

[4] Curtius and Dedichen, *J. prakt. Chem.*, [2] **50**, 266 (1894).

[5] Brady and Elsmire, *Analyst*, **51**, 77 (1926).

in the experimental part. The melting points of some derivatives are not far enough apart to be characteristic but this is of minor importance, since it is now customary to prepare a known sample for comparison and make a determination of a mixed melting point. A few substances did not give solid products—these are listed in the experimental part.

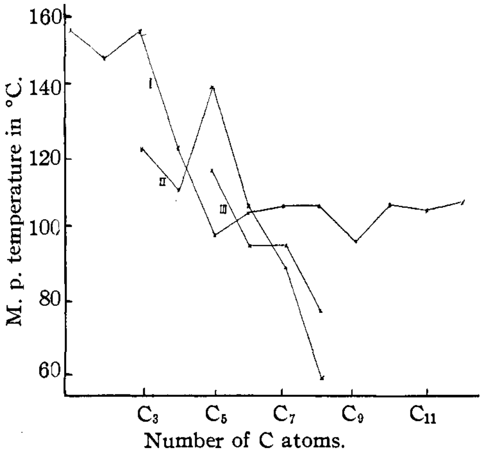


Fig. 1.

In the accompanying figure are shown the melting points of three series of dinitrophenylhydrazones plotted against the number of carbon atoms in the aliphatic part of the molecule. Curve I represents the straight-chain aldehydes, II the methyl ketones with a straight chain, and III the methyl ketones with a branched chain of the *iso* type (branching on the carbon atom farthest from the carbonyl group). The well-known alternating effect is noticeable, even though the series is short.[6]

Experimental

Preparation of 2,4-Dinitrophenylhydrazine.—Fourteen g. of hydrazine sulfate is suspended in 50 cc. of hot water in a 125-cc. beaker, stirred well, and 35 g. of potassium acetate added to precipitate the sulfate as potassium sulfate. After boiling for five minutes, it is cooled somewhat and 30 cc. of alcohol added. When cold, the solid is filtered by suction and the cake washed while on the funnel with 25 cc. of hot alcohol. In a flask fitted with a reflux condenser and stirrer is dissolved 20.2 g. of technical 2,4-dinitrochlorobenzene in 100 cc. of alcohol, the hydrazine solution as prepared above is added and the whole refluxed with stirring for an hour. Most of the product crystallizes out after ten minutes. It is filtered, after cooling, and washed once with 25 cc. of warm alcohol to remove any unchanged dinitrochlorobenzene, and then with a small amount of warm water to remove soluble salts. By evaporating the filtrate to half its volume, a further 5 g. may be obtained, making the total yield 17 g. or 85%. The first crystals, m. p. 192°, are sufficiently pure for use as a reagent, but the last should be recrystallized from ethyl acetate.

Substitution of sodium hydroxide for potassium acetate slows up the reaction and gives an inferior product. This method avoids the preparation of concentrated solutions of hydrazine hydrate, though the latter gives a slightly better yield. The same yields can be secured with two and a half times the above amounts, if well stirred during the refluxing.

Of the several methods that can be devised for preparing 2,4-dinitrophenylhydrazones, we used the following.

A.—For qualitative identification of small amounts: A saturated solution of dinitrophenylhydrazine is prepared by refluxing 1 g. of the solid with 100 cc. of alcohol;

---

[6] For example, *cf.* Malone and Reid, This Journal, 51, 3424 (1929).

it may partially crystallize on cooling. To 5 cc. of this solution (any suspended solid does no harm) in a test-tube is added 5 cc. of alcohol and a few drops of the carbonyl compound, and the whole carefully heated to boiling. After removing from the flame, 1–2 drops of concd. hydrochloric acid are slowly added; the color usually changes immediately to yellow or orange. The mixture is boiled for two minutes, and water added, drop by drop, to incipient cloudiness or crystallization. The dinitrophenylhydrazone is filtered after the solution is cold. If the aldehyde or ketone is fairly pure, recrystallization is unnecessary, but the products separating when commercial preparations are used are always impure. Alcohol is the best solvent for the low-melting derivatives, but the higher-melting less soluble compounds require the addition of ethyl acetate or chloroform. The dinitrophenylhydrazones of the simple ketones (except acetone and methyl ethyl ketone) separate slowly from alcohol, but usually form as oils on addition of water. If the solution is heated too long when acrolein is used, polymerization of some sort occurs and a viscous tar is precipitated.

B.—For preparing larger quantities, 2 g. of dinitrophenylhydrazine and a slight excess over the equivalent amount of carbonyl compound in 100 cc. of alcohol are heated to boiling, allowed to cool slightly and 2 cc. of concd. hydrochloric acid added. Usually the color changes at once, and any solid present dissolves. After boiling for two minutes, the solution is set aside until crystallization is complete, filtered by suction, washed with alcohol and recrystallized to constant melting point.

The reagent is not as useful when applied to α-hydroxy ketones of the acyloin and benzoin type; the formation of hydrazone is slow; unchanged material precipitates on addition of water. If the boiling is prolonged, oxidation takes place,[7] and the mixture of solid products formed is not easily separated by recrystallization. Since benzoin, benzil, and their homologs are solids this limitation is unimportant; however, not many crystalline derivatives of the liquid acyloins are known. After several recrystallizations a solid, m. p. 99°, was obtained from *n*-butyroin, but its structure is uncertain.[8]

It is essential that the carbonyl compounds be fairly pure; otherwise purification of the phenylhydrazones is difficult. For example, it was extremely difficult to purify the crystalline products formed from some samples of *n*-decylaldehyde and menthone.

The compounds used were either purchased from reliable sources or prepared by methods already in the literature.

TABLE I

RESULTS OF EXPERIMENTS

Ketones	M. p., °C.	Color	Aldehydes	M. p., °C.	Color
Acetone[4]	128	Y	Formaldehyde[3]	155	Y
Methyl ethyl[5]	115	Y	Acetaldehyde[3]	147	Y
Methyl *n*-propyl	141	YO	Propion-[5]	155	Y
Methyl *n*-butyl	106	RO	*n*-Butyr-[5]	122	Y
Methyl *n*-amyl	89	YO	Isobutyr-[5]	182	Y
Methyl *n*-hexyl	58	O	*n*-Valer-	98	Y
Methyl *n*-nonyl	63	OY	Isovaler-[5]	123	Y
Methyl *n*-undecyl	69	OY	Trimethylacet-[5]	210	Y
Methyl isopropyl	117	OY	*n*-Capro-[5]	104	Y
Methyl isobutyl	95	OR	*n*-Hept-[5]	106	Y
Methyl iso-amyl	95	O	*n*-Oct-	106	Y
Methyl isohexyl	77	OY	*n*-Nonyl-[5]	96	Y

---

[7] Thus both piperoin and piperil give the same substance, m. p. 227°.

[8] Analysis for nitrogen gave 14.5 and 14.3, whereas the calculated value for the monophenylhydrazone is 17.2%, and for the osazone 22.1%.

TABLE I (*Concluded*)

Ketones	M. p., °C.	Color	Aldehydes	M. p., °C.	Color
Pinacolone	125	OY	*n*-Decyl-	104	Y
Diethyl	156	WO	*n*-Undecyl-	104	Y
Di-*n*-propyl	75	YO	*n*-Duodecyl-	106	Y
Ethyl *n*-propyl	130	YO	Acrolein	165	RO
Ethyl isobutyl	75	YO	α-Methyl-β-ethyl acrolein	159	Carmine
Allylacetone	104	O	Citronellal	78	Y
Methylheptenone	81	RO	Citral I	108–110	RO
Pseudoionone	143	Deep red	Citral II	96	RO
Mesityl oxide	200	Carmine	α-*n*-Amylcinnamic aldehyde.	164	Scarlet
Cyclopentanone	142	OY	Acid derivatives[c]		
Cyclohexanone[a]	160	OY	Pyruvic acid	213	Lemon
Methyl cyclohexyl	140	O	Levulinic acid	92	Y
Carvone	189	Carmine	Ethyl oxomalonate	128	Lemon
Menthone	145	O	Methyl benzoyl formate	171	OY
Benzalacetone	223	OR			
Benzalacetophenone	208	O			
Benzil[b]	185	OY			
Acetophenone	237	O			
α-Indanone	258	RO			
n-Butyroin	99	Y			
Benzoin	234	OY			

This substance has previously been reported[9] with m. p. 145°. [b] For this substance we are indebted to Mr. A. Paquet. [c] The reagent gives no precipitate with formic acid and the formates.

The results obtained with furoin, furil and benzfuroin were unsatisfactory. Furfural is reported to give a solid, m. p. 202°.[9] Anisoin, anisil, piperoin and piperil gave mixtures melting above 200°.

Representative samples were analyzed for nitrogen by the Kjeldahl method, on a semi-micro scale. A mixture made up of 0.030 g. of substance, 0.1 g. of copper sulfate, 2 g. of potassium sulfate, 2 g. of glucose and 15 cc. of concd. sulfuric acid was digested until colorless. After cooling, it was carefully diluted with 150 cc. of distilled water, a 24-g. stick of solid sodium hydroxide added, and the ammonia distilled in the usual manner. It was found most convenient to weigh the sample on a cigarette paper, and

TABLE II[a]

KJELDAHL ANALYSES

C=O compound	Nitrogen, % Calcd.	Found
n-Octaldehyde	18.1	18.3
Pinacolone	20.0	19.7
Methyl isohexyl ketone	18.1	18.1
Cyclohexanone	20.1	20.0
Citral II	16.5	16.5
Pseudoionone	15.1	14.9
α-*n*-Amylcinnamic aldehyde	14.9	15.1
Benzalacetone	14.5	14.7

[a] For these analyses we are indebted to Mr. D. D. McKay.

---

[9] Ciusa, *Gazz. chim. ital.*, **41**, 688 (1911); *Chem. Zentr.*, **82**, 1644 (1911).

put the whole into the flask; of course, a paper was used in running a blank. Sodium hydroxide, 0.020 *N* and sulfuric acid, 0.040 *N* were of suitable strength. This method does not require as much skill as Pregl's micro method, nor as large a sample as the usual procedure. Senior students used it with good results.

2,4-Dinitrophenylhydrazine did not give solid derivatives with methyl *n*-heptyl, *n*-octyl, and *n*-decyl ketones, di-*n*-butyl ketone, commercial ionone, pure α-ionone, fenchone or pulegone.

Summary

1. An inexpensive method is given for the preparation of 2,4-dinitrophenylhydrazine.

2. This substance has been shown to be a suitable reagent to use in preparing crystalline derivatives of a large number of aliphatic compounds containing a carbonyl group. It may also be used with certain cyclic compounds, but the production of solid derivatives is not as general.

3. It is not as useful with α-hydroxyketones, owing to the difficulty in separating the mixtures formed.

4. A semi-micro method for determining nitrogen by the Kjeldahl method is outlined.

MONTREAL, CANADA

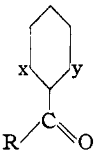
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STUDY OF THE POSSIBLE ISOMERISM OF CERTAIN ANALOGS OF RESOLVABLE DIPHENYL COMPOUNDS. VII[1]

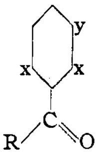
BY R. W. MAXWELL[2] AND ROGER ADAMS

RECEIVED MARCH 28, 1930 PUBLISHED JULY 3, 1930

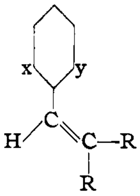
It was pointed out in a previous paper[1a] that certain substances somewhat similar to diphenyl compounds might show the phenomenon of optical isomerism which exists in the ortho tri, and tetra-substituted members of the former class of compounds. These general types are given in formulas I to VI.



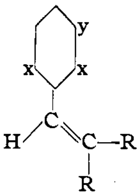
I



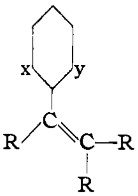
II



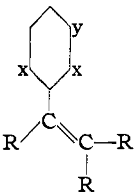
III



IV



V



VI

---

[1] For previous papers see (a) Hyde and Adams, THIS JOURNAL, **50,** 2499 (1923); (b) Moyer and Adams, *ibid.*, **51,** 630 (1929); (c) Stanley and Adams, *Rec. trav. chim.*, **48,** 1035 (1929); (d) Stanley and Adams, THIS JOURNAL, **52,** 1200 (1930); (e) Bock, Moyer and Adams, *ibid.*, **52,** 2054 (1930); (f) Stearns and Adams, *ibid.*, **52,** 2070 (1930).

[2] This communication is a portion of an abstract of a thesis submitted by R. W. Maxwell in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.