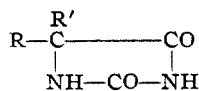
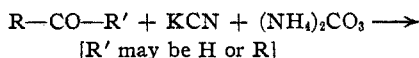


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Identification of Carbonyl Compounds through Conversion into Hydantoins¹BY HENRY R. HENZE AND ROBERT J. SPEER²

For the qualitative identification of a liquid organic compound, the attempted conversion of the latter into a solid derivative has become a routine procedure. To serve this purpose it is desirable that the derivative should be formed readily and in good yield, in order that a small amount of material should suffice for positive characterization, be purified easily, and possess a sharp melting point. For the recognition of a carbonyl compound, especially of one of the simpler or better-known ketones and aldehydes, resort is usually made to the preparation of an oxime, semicarbazone, phenylhydrazone, mono- or di-substituted phenylhydrazone, or aldimethone. Of course every carbonyl compound does not form a solid derivative of each of these types, and the choice of organic reagent to be used may depend upon the availability of one or another of the appropriate organic reagents. Hence, additional reagents, capable of reacting with the majority of carbonyl compounds to form solid derivatives, of the less expensive and, perhaps, more readily available inorganic chemical type, are desirable.

By reason of our investigation of the synthesis and properties of bifunctional aliphatic compounds, we have had opportunity to study the activity of the carbonyl group in keto ethers. It has been observed that hydantoins were prepared from certain of these substituted ketones even though the latter did not form solid derivatives of any of the types mentioned previously. We have adopted the method first described by Bucherer and Lieb³ in which the carbonyl compound is warmed in dilute alcoholic solution with potassium (or sodium) cyanide and ammonium carbonate. In many instances the hydantoin sepa-



rates from the warm solution in a state of such

purity that subsequent recrystallization raises the melting point scarcely at all. The method is not useful in the case of formaldehyde, certain unsaturated aldehydes, a few (but not all) hydroxy- and nitro-aryl aldehydes, bis-(dimethylamino)-acetone, and pyruvic acid. However, levulinic acid and ethyl acetoacetate are converted readily into the corresponding 5,5-disubstituted hydantoins.

We have tested the applicability of this procedure by conversion into hydantoins of twenty-four common aldehydes, thirty-six common ketones and about fifty less common carbonyl compounds.⁴ The thirty-nine more common carbonyl compounds which have been converted by us into hydantoins by this method are listed, together with the melting point of each hydantoin, in Table I.

General Procedure for Hydantoin Preparation.—Two-hundredths mole of ketone, or about 2 g. of a carbonyl derivative of unknown constitution, is dissolved in 50 cc. of 50% alcohol, and 9.1 g. (0.08 mole) of ammonium carbonate and 2.6 g. (0.04 mole) of potassium cyanide added. This mixture is warmed under a condenser at a temperature of 58–60° for two hours, the solution concentrated to approximately two-thirds of the initial volume and chilled in an ice-bath. Except in the case of the hydantoins of lowest molecular weight, which are quite soluble in water, the hydantoin will separate at this point in the form of minute white or faintly yellow crystals. If, however, no separation of hydantoin occurs, subsequent acidification with hydrochloric acid [Hood!!] and further chilling usually suffices to precipitate the hydantoin. As a last resort, in the case of the very water-soluble derivatives, the acidified mixture is evaporated to dryness under diminished pressure and the residue extracted several times with boiling benzene, from which the hydantoin can be obtained as an amorphous powder. In general, the hydantoins are very pure even when taken directly from the reaction mixture, and subsequent recrystallizations seldom raise the melting point appreciably. In those cases where purification was necessary, the hydantoin was dissolved in aqueous alcoholic solution, the latter decolorized with Norite, and the derivative obtained in a colorless condition.

Time Determinations.—Acetophenone was used as the "indicator" compound in deter-

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(3) Bucherer and Lieb, *J. prakt. Chem.*, **141**, 5 (1934).

(4) The complete list of carbonyl compounds which have been converted into hydantoins as a means of identification through the procedure outlined in the experimental portion of this paper, has been deposited with the American Documentation Institute, 2101 Constitution Ave., Washington, D. C., and is available as American Documentation Institute Document No. 1603, on remittance of 25¢ for microfilm or 70¢ for photocopies.

TABLE I
CARBONYL COMPOUNDS IDENTIFIED INITIALLY IN THIS
INVESTIGATION THROUGH CONVERSION INTO THE HYDAN-
TOIN DERIVATIVE^o

Compound	M. p., °C. (cor.) ^b	Nitrogen, %	
		Calcd.	Found
<i>n</i> -Amyl methyl ketone	102.5-103.5	15.21	15.46
<i>n</i> -Hexyl methyl ketone	107.5-108.0	14.13	14.17
<i>n</i> -Butyl methyl ketone	107.5-108.5	16.46	16.44
Methyl <i>n</i> -propyl ketone	123.0-124.5	17.94	17.72
<i>n</i> -Valeraldehyde	139.5	17.94	17.81
<i>n</i> -Hexaldehyde	144.5	16.46	16.50
Ethyl <i>n</i> -propyl ketone	144-145	16.46	16.52
Furfuraldehyde	147	16.87	17.04
<i>n</i> -Heptaldehyde	148	15.21	15.18
Isobutyl methyl ketone ^h	148	16.46	16.56
Isoamyl ethyl ketone	153	14.13	14.34
Levulinic acid	156.5-157.5	15.05	14.85
Citronellal	172.0-172.5	12.55	12.65
<i>n</i> -Butyl <i>n</i> -propyl ketone	175	14.13	14.00
Diethylacetaldehyde ^f	175.7-176.1	16.46	16.51
<i>o</i> -Chlorobenzaldehyde	176	16.84 ^c	16.94 ^c
Methyl isopropyl ketone	177	17.94	17.90
<i>p</i> -Tolualdehyde	182.5	14.73	14.61
Veratraldehyde	182.5-183.0	11.86	12.04
<i>o</i> -Ethoxybenzaldehyde	185-186	12.72	12.71
<i>o</i> -Methoxybenzaldehyde	186-187	13.59	13.55
Carvone ^d	193.5-194.0	17.00	17.20
Mesityl oxide ^h	194	16.66	16.71
Methyl <i>p</i> -tolyl ketone	203.5	13.72	13.55
Cyclopentanone ^g	204-205	18.17	18.27
Piperonaldehyde	207	12.73	12.63
Diisopropyl ketone	207	15.21	15.51
<i>p</i> -Methoxyphenyl methyl ketone	210	12.72	12.57
<i>m</i> -Hydroxybenzaldehyde	212	14.58	14.66
Isovaleraldehyde ^g	212.5-216.0	17.94	18.00
2-Methylcyclohexanone ^g	215.5-216.0	15.31	15.61
<i>p</i> -Dimethylamino- benzaldehyde	234-235	19.17	18.96
α -Hydrindone	240	13.86	13.91
Thujone	254.5-255.0	12.61	12.75
<i>p</i> -Hydroxybenzaldehyde	263 dec.	14.58	14.47
3-Methylcyclohexanone ^g	268.5-269.0	15.31	15.61
Vanillin	276 dec.	12.61	12.34
4-Methylcyclohexanone	279-280	15.31	15.40
Fluorenone ^e	324-325 dec.	11.11	11.15

^o The hydantoin derived from the simpler, or better-known aldehydes and ketones usually may be named readily as 5-mono-substituted and 5,5-disubstituted hydantoin, respectively.

This system of nomenclature becomes unduly cumbersome in the case of hydantoin formed from aldehydes and ketones of the terpene series or from polycyclic ketones. Derivatives of the latter type are best termed as spirohydantoin. Thus, thujone yields 1-isopropyl-4-methylspiro[bicyclo[3.1.0]hexane-3,4'-imidazolidine]-2',5'-dione or, more simply, "thujonespirohydantoin"; α -hydrindone forms spiro-(indan-1',5-hydantoin) or " α -hydrindone-spirohydantoin"; fluorenone is converted into spiro(fluorene-9,4'-imidazolidine)-2,5-dione or "fluorenone-spirohydantoin." The aid of Drs. L. T. Capell and A. M. Patterson in naming several of our more complex hydantoin derivatives is gratefully acknowledged.

^b All melting points represent corrected temperatures. ^c Represents percentage of chlorine. ^d The derivative formed from carvone is a cyano compound, namely, 2,4-dioxo-6-methyl-9-isopropenyl-1,3-diazaspiro[4,5]decane-7-carbonitrile. ^e D. D. Humphries with Henze, unpublished data. ^f A. Nease with Henze, unpublished data. ^g Eric Smith with Henze, unpublished data. ^h Thomas R. Thompson with Henze, unpublished data.

mining the most satisfactory time for reaction. The following results were obtained, from which the two-hour period of warming was chosen.

Expt.	Time	Temp., °C.	Crude product, g.	M. p. of product, °C.	Yield, %
1	1 hour	55-60	1.6	198	42
2	2 hours	55-60	2.1	198	55
3	3 hours	55-60	2.3	198	61

Very similar results were obtained using acetone, although in this case greater difficulty was experienced in isolation of the more water-soluble hydantoin.

Summary

Identification of carbonyl compounds in a satisfactory manner can be effected from readily available inorganic compounds by conversion of the carbonyl compound into a hydantoin by interaction with potassium cyanide and ammonium carbonate. The melting point of the hydantoin derived from each of thirty-nine carbonyl compounds is tabulated.

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