column with 150 ml. of 5% potassium hydroxide solution. This effluent was neutralized with sulfuric acid, buffered with solid sodium hydrogen carbonate, cooled and analyzed for periodate by the usual arsenite-iodine procedure.[14]

Catechol. Commercial catechol was recrystallized from toluene. The reaction mixture was 9.94×10^{-3} molar in periodic acid and 1.80×10^{-3} molar in catechol (initial ratio of reactants 5.52/1). A moderate orange color developed immediately, and did not change noticeably after the first few minutes.

Guaiacol. Redistilled, center cut, b.p. 205°. Periodic acid $9.92 \times 10^{-3}M$, guaiacol $1.99 \times 10^{-3}M$, reactant ratio 4.98/1. When the reactants were mixed a yellow color developed quickly. However, in less than three minutes the solution was indistinguishable from the catechol-periodate mixture described above.

Pyrogallol. Commercial C. P. grade, m.p. 131–133°. Periodic acid $9.92 \times 10^{-3}M$, pyrogallol $1.98 \times 10^{-3}M$, reactant ratio 4.99/1. A deep brown color developed quickly when the reactants were mixed. In time the color became less pronounced and approached that of the two mixtures described above.

Resorcinol. Recrystallized from benzene, m.p. 110°. Periodic acid $9.97 \times 10^{-3}M$, resorcinol $1.26 \times 10^{-3}M$, reactant ratio 7.89/1. There was no color change on mixing the reactants.

Resorcinol monomethyl ether. Redistilled, center cut, b.p. 128–128.5°/13. Periodic acid $9.90 \times 10^{-3}M$, compound $1.85 \times 10^{-3}M$, reactant ratio 5.35/1. A light yellow color slowly developed when the reactants were mixed.

Phloroglucinol. Recrystallized from hot water and dried to constant weight *in vacuo* at 65°. This process yields anhydrous phloroglucinol. Periodic acid $9.97 \times 10^{-3}M$, phloroglucinol $8.72 \times 10^{-4}M$, reactant ratio 11.4/1. No color change observed on mixing.

Hydroquinone. Recrystallized from water, m.p. 161°. Periodic acid $9.94 \times 10^{-3}M$, hydroquinone $2.06 \times 10^{-3}M$, reactant ratio 4.83/1. A light yellow color quickly developed upon mixing.

Hydroquinone monomethyl ether, m.p. 54°. Periodic acid $9.90 \times 10^{-3}M$, compound $1.88 \times 10^{-3}M$, reactant ratio 5.26/1. The reaction mixture was yellow after 24 hr., slowly changed to brown, and finally became cloudy.

Phenol. Redistilled center cut, b.p. 181°. Periodic acid $9.80 \times 10^{-3}M$, phenol $3.06 \times 10^{-3}M$, reactant ratio 3.20/1. The solution turned light yellow on mixing the reactants and after 24 hr. became cloudy.

Veratrole. Redistilled center cut, b.p. 205°. Periodic acid $9.92 \times 10^{-3}M$, veratrole $1.89 \times 10^{-3}M$, reactant ratio 5.25/1. Light yellow solution produced on mixing the reactants.

Acknowledgment. We wish to express our appreciation to the Research Corporation and to the E. I. du Pont de Nemours Co. for grants to the Bucknell University Chemistry Department which made this work possible. Some of the preliminary experiments were carried out by Mr. Donald Dietz.

LEWISBURG, PA.

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

Use of Nuclear Magnetic Resonance to Distinguish between Aliphatic Aldehyde and Ketone Derivatives

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The use of nuclear magnetic resonance to differentiate between aldehyde and ketone semicarbazones and 2,4-dinitrophenylhydrazones is described. The proton resonance of the N=C—H group of methylene chloride solutions of the dinitrophenylhydrazones occurs at −109 to −118 c.p.s. (at 40 Mc. relative to water as zero) and the corresponding resonance frequency of the semicarbazones is at −86 to −97 c.p.s. (40 Mc. relative to water) in the series of compounds studied. Other features of the NMR spectra are also discussed.

It has long been possible to distinguish aldehydes from ketones by standard chemical methods. In more recent years differences in physical properties, for example, differences in the carbonyl stretching frequency or the occurrence of the aldehydic C–H stretching band in infrared spectra, have been widely employed for the same purpose. However, in certain instances aldehydes and ketones, frequently liquids and obtained in low yield as degradation products, often from ozonolyses, can be isolated conveniently only as their derivatives. It is desirable, therefore, to have a method of determining whether such a derivative originated from an aldehyde or a ketone.

Ultraviolet[1–3] and infrared[2] spectral methods have been employed previously for this purpose. Thus, aldehyde 2,4-dinitrophenylhydrazones have been shown, in general, to have ultraviolet maxima at somewhat shorter wavelengths than those of similar derivatives of ketones,[1,2] while the color of the aldehyde derivatives deteriorated faster in basic solution than did that of the ketone derivatives.[2] In the infrared spectra of the dinitrophenylhydrazones of most compounds investigated the N–H stretching band was found at higher frequency in the ketone derivatives than in the aldehyde derivatives.[2] These correlations have proved useful; however, the shifts are slight and in marginal cases the ultraviolet and infrared spectral bands are

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[1] G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953).

[2] L. A. Jones, J. C. Holmes, and R. B. Seligman, *Anal. Chem.*, **28**, 191 (1956).

[3] A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, 2nd ed., Edward Arnold, Ltd., London, 1958, p. 60.

TABLE I

NMR PEAKS OF 2,4-DINITROPHENYLHYDRAZONES

2,4-Dinitrophenylhydrazone[a] of	Peaks (c.p.s.)[b]							
	A	B				C	D	E
Acetaldehyde	−258	−174	−149	−139	−131	−118	−114	
		−171	−146	−137	−121	−113	+ 65	
Propionaldehyde	−250	−174	−148	−139	−131	−115	−113	
		−172	−146	−136	−121	−110	+ 67	
n-Butyraldehyde	−241	−168	−144	−135	−127	−113	−111	
		−165	−141	−133	−117	−108	+ 69	
Enanthaldehyde	−244	−172	−147	−140	−131	−114	−114	
		−169	−144	−138	−121	−109	+ 66	
Isobutyraldehyde	−249	−173	−149	−139	−130	−114	−113	
		−170	−147	−137	−120	−109	+ 69	
α-Ethylbutyraldehyde	−252	−172	−147	−139	−130	−110	−112	
		−171	−144	−136	−120	−104	+ 65	
Hydratropaldehyde	−244	−169	−144	−135	−127	−114	−107	−98
		−166	−141	−132	−117	−109	+ 71	
Acetone	−245	−173	−147	−137	−128		−112	
		−170	−144	−134	−118		+ 68	
Methyl ethyl ketone	−245	−169	−145	−136	−128		−110	
		−167	−142	−133	−119		+ 67	
Pinacolone	−244	−169	−145	−136	−128		−109	
		−167	−143	−132	−118		+ 68	
Cyclopentanone	−239	−171	−145	−137	−126		−113	
		−168	−142	−134	−116		+ 67	
4-Methylcyclohexanone	−248	−169	−144	−135	−128		−112	
		−166	−141	−132	−118		+ 65	
Benzylacetone	−245	−171	−146	−136	−126		−111	−99
		−169	−141	−134	−116		+ 70	
Methylene chloride							−112	
							+ 63	

[a] Methylene chloride solutions, concentrations found in Experimental section. [b] At 40 Mc., relative to water as zero. Peak interpretations are as follows: A, —NH—; B, 2,4-dinitrophenyl H's (*cf.* footnote 6 to text); C, —CH=N—; D, $^{13}CH_2Cl_2$ (solvent); E, phenyl H's.

difficult to assign with certainty to aldehyde or ketone starting materials.

An alternative method is one based on nuclear magnetic resonance spectroscopy, which may be expected *a priori* to offer advantage, since this method depends only on the presence or absence of the aldehyde hydrogen in the derivative. The present study was undertaken to determine the applicability and convenience of NMR spectroscopic methods in distinguishing between derivatives of aliphatic aldehydes and ketones. The hydrogen atom of the aldehyde functional group has been shown previously to give rise to resonance in the region −180 to −200 c.p.s. (relative to water as zero at 40 Mc.)[4a] while the substrate aldehyde proton resonance (—CH=N—) has been found at −88 and −62 c.p.s. for *syn* and *anti* forms of aldoximes (*cf.* below).[4b] It was hoped that the position of this hydrogen resonance would be equally distinctive in the semicarbazone and dinitrophenylhydrazone derivatives.

In the present investigation the NMR spectra of a number of aliphatic aldehyde and ketone 2,4-dinitrophenylhydrazones and semicarbazones have been determined in methylene chloride solution at 40 Mc.[5] Four of these spectra are presented in Fig. 1 and significant peaks of these four and other carbonyl derivatives are summarized in Tables I and II. In substantiation of expectation the NMR spectra of these derivatives conclusively distinguish between aldehyde and ketone substrate.

With the resolution available the aldehyde proton absorption appears as a doublet, due to H–H splitting (J_{HH} value 5–6 c.p.s.), in those dinitrophenylhydrazone and semicarbazone derivatives investigated (Tables I and II, Column C). For the dinitrophenylhydrazones the peaks are found in the region −104 to −118 c.p.s. and for the semicarbazones in the region −86 to −97 c.p.s. The appearance of these peaks readily distinguishes the

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(4) (a) L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953); (b) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958).

(5) This study has been restricted to aliphatic compounds since the corresponding aromatic aldehyde and ketone derivatives were difficultly soluble in methylene chloride; similarly, the 2,4-dinitrophenylhydrazone and semicarbazone of formaldehyde were relatively insoluble. Spectra were determined, where possible, of 20% solutions of the derivatives, while lower concentrations gave less satisfactory spectra. However, no intrinsic limitation of utility to the aliphatic series is implied. The position of the substrate aldehyde hydrogen of conjugated unsaturated and aromatic aldehyde dinitrophenylhydrazones and semicarbazones might be expected to be in a position not far removed from that of the corresponding saturated aldehyde derivatives since position of the aldehyde hydrogen is essentially the same in saturated, unsaturated. and aromatic aldehydes.[4a]

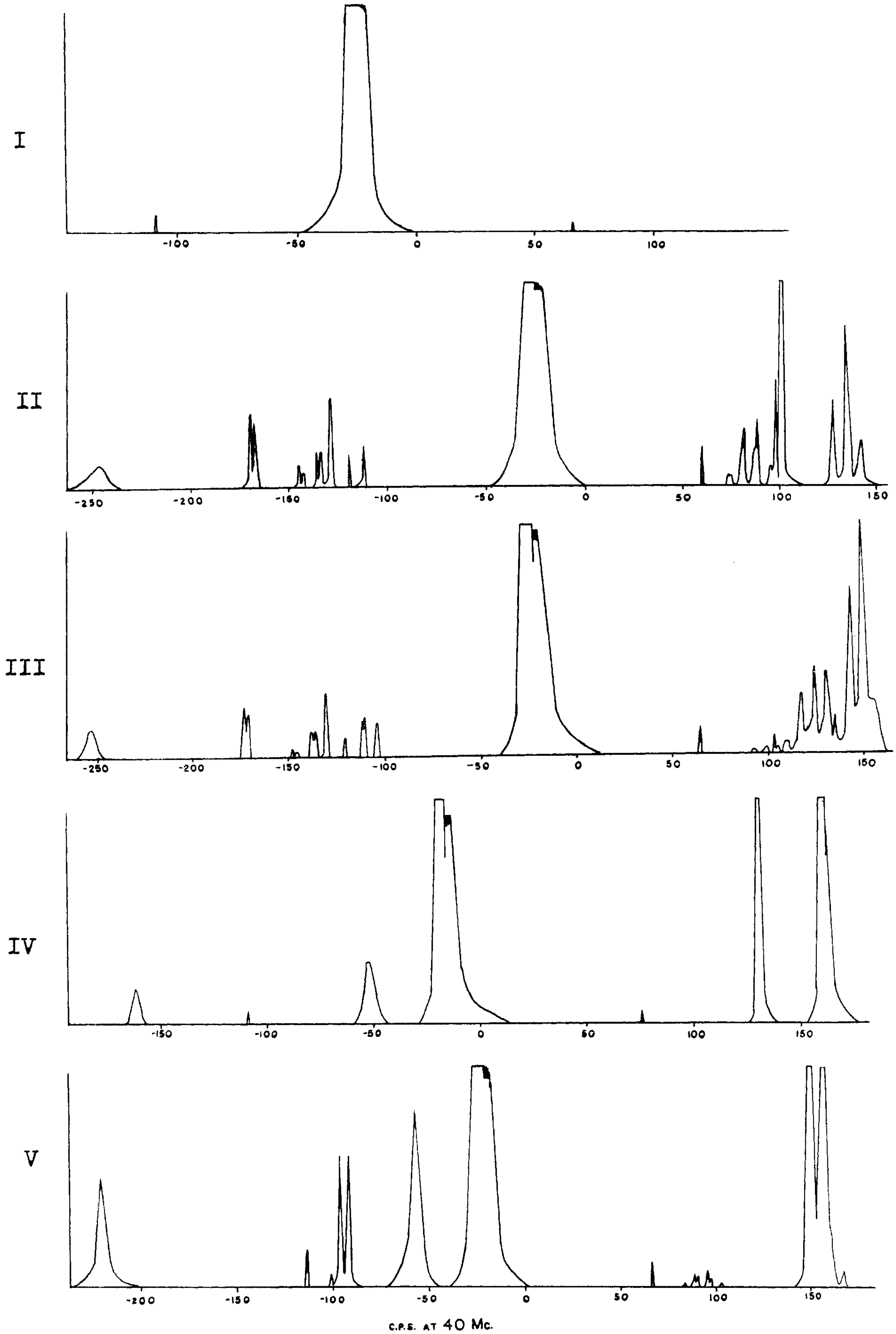

Fig. 1. NMR spectra of aldehyde and ketone derivatives. I. Methylene chloride solvent. II. Methyl ethyl ketone 2,4-dinitrophenylhydrazone. III. α-Ethylbutyraldehyde 2,4-dinitriphenylhydrazone. IV. Pinacolone semicarbazone. V. Isobutyraldehyde semicarbazone

TABLE II

NMR PEAKS OF SEMICARBAZONES

Semicarbazone[a] of	Peaks (c.p.s.)[b] A	B	C	D
Isobutyraldehyde	−209	−112	−97	−57
		+ 63	−92	
α-Ethylbutyraldehyde	−210	−112	−92	−58
		+ 64	−86	
Methyl *n*-amyl ketone	−164	−115		−48
		+ 68		
Di-*n*-butyl ketone	−165	−113		−54
		+ 67		
Pinacolone	−161	−114		−53
		+ 65		

[a] Methylene chloride solutions, concentrations found in Experimental section. [b] At 40 Mc., relative to water. Peak interpretations are as follows: A, —NH—; B, $^{13}CH_2Cl_2$ (solvent); C, —CH=N—; D, NH_2.

spectra of the aldehyde derivatives from those of the corresponding ketone compounds (*cf.* Fig. 1). It is of interest that the —CH=N—proton absorption (multiplet) is found only in a single narrow region; hence, it may be assumed that the 2,4-dinitrophenylhydrazones and semicarbazones studied exist in a single isomeric form (*syn* or *anti*), in contrast to oximes, which were shown[4b] to exist in both *syn* and *anti* forms, of differing chemical shifts (at −88 and −62 c.p.s., respectively).

The semicarbazone spectra are somewhat simpler and more useful in distinguishing substrate types since they have no interfering aromatic protons absorbing in the same region (Table I, Column B) with the aldehyde proton, while the dinitrophenylhydrazones exhibit a total of eight peaks in the region at slightly lower field than that of the aldehyde substrate hydrogen.[6] The utility of the semicarbazone derivatives is limited, however, by their relatively low solubility in methylene chloride compared to the solubility of the 2,4-dinitrophenylhydrazones.

An additional peak in the same region as that of the aldehyde dinitrophenylhydrazone proton is due to the natural abundance (1%) of ^{13}C in the solvent methylene chloride.[7] This absorption occurs as a pair of satellite bands near −112 and +67 ($J_{^{13}CH}$ = 179 c.p.s.). Other readily assigned proton peaks at field values negative relative to that of water include broad —NH —proton absorption, in the regions −241 to −258 for dinitrophenylhydrazones, −210 for aldehyde semicarbazones, −163 for ketone semicarbazones, and broad —NH_2 proton absorption in the region −48 to −58 for the semicarbazones. The assignment of peaks is strengthened by the relative intensities of the bands. For example, in the spectrum of isobutyraldehyde semicarbazone (Fig. 1, Curve V) the —NH— peak at −209, the split —CH=N— peaks at −97 and −92, and the —NH_2 peak at −57 c.p.s. have relative intensities of 1:1:2, respectively.

Aromatic phenyl proton absorption was found at −99 c.p.s. in the spectra of dinitrophenylhydrazones of phenyl-substituted aldehydes and ketones. This band would be likely to overlap the absorption of the —CH=N— proton in semicarbazones; hence the maximal utility of semicarbazone spectra is restricted to aliphatic compounds. The —NH— and —NH_2 bands do not interfere with the assignment of the dinitrophenylhydrazones or semicarbazones as aldehyde or ketone derivatives, nor do the dinitrophenyl or methylene chloride satellite peaks described above when the spectrum of an unknown is compared to that of model compounds. Hence, the NMR spectra of these derivatives are definitive and useful criteria in assessing the nature of the substrate carbonyl compound.

EXPERIMENTAL[8]

2,4-Dinitrophenylhydrazones and semicarbazones were prepared by standard procedures;[9] melting points are reported in Tables III and IV.

NMR spectra of 2,4-dinitrophenylhydrazones and semicarbazones were calibrated in c.p.s. at 40 Mc. Samples were spun in a precision annular cell and an external sample of chloroform (−104 c.p.s.), benzene (−76 c.p.s.) or water (0 c.p.s.) was used for the calibration point in each spectrum. A Varian Associates Model V-4300-C high resolution *NMR* spectrometer with a 12-inch magnet and VK-3506 flux stabilizer was used to determine the spectra. Audio-frequency sidebands were generated with a Hewlett-Packard 200-CD audio-oscillator.

Methylene chloride was used as the solvent for both the 2,4-dinitrophenylhydrazones and the semicarbazones. The concentrations of the 2,4-dinitrophenylhydrazone solutions were 20% (weight/volume) with the following exceptions: acetaldehyde (9%), propionaldehyde (13%), enanthalde-

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(6) Professor H. S. Gutowsky (personal communication) has interpreted the various dinitrophenyl peaks in terms of the following spin-spin splitting values: the C-3 proton, at a position *ortho* to both nitro groups, shows the greatest chemical shift but only small splitting (J_{HH} 2–3 c.p.s.) since it is split only by the proton *meta* to it (typical values, −171, −168), all splitting by *para* protons neglected; the C-6 proton, at a position *meta* to both nitro groups, shows the least chemical shift but larger splitting (J_{HH} 9–10 c.p.s.) since it is split by the proton *ortho* to it (typical values, −128, −118); the C-5 proton, at a position *ortho* to one nitro group and *para* to the other, shows an intermediate chemical shift with a small splitting constant (J_{HH} 2–3 c.p.s.) due to splitting by the proton *meta* to it, superimposed on a larger splitting constant (J_{HH} 9–10 c.p.s.) due to splitting by the adjacent *ortho* proton (typical values, −147, −144, −137, −134). We are indebted to Professor Gutowsky for this interpretation [*cf.* also H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957)].

(7) (a) A. D. Cohen, N. Sheppard, and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958); (b) H. S. Gutowsky, unpublished results.

(8) All melting points are corrected. The NMR spectra were obtained by Mr. B. A. Shoulders. The reproductions in Fig. 1 are tracings of the original spectra with the base lines adjusted to coincide with the bottoms of the tracings.

(9) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley and Sons, Inc., New York, 1956, pp. 218–19.

TABLE III

Melting Points of 2,4-Dinitrophenylhydrazones

2,4-Dinitrophenylhydrazone of	M.P., °C. Found	M.P., °C. Reported	Reference
Acetaldehyde	148–148.5	147 (162)	10
Propionaldehyde	147–148	154	10
n-Butyraldehyde	122–123	122	10
Enanthaldehyde	106.0–106.5	106	10
Isobutyraldehyde	182–183	182	10
α-Ethylbutyraldehyde	94–95	94	11
Hydratropaldehyde	136–137	136–137	12
Acetone	126–127	126	13
Methyl ethyl ketone	118–119	115	10
Pinacolone	126–127	125	16
Cyclopentanone	146–146.5	146–147	13
4-Methylcyclohexanone	133.5–134.0	134.7–135.1	15
Benzylacetone	127–128	125–126.3	14

TABLE IV

Melting Points of Semicarbazones

Semicarbazone of	M.P., °C. Found	M.P., °C. Reported	Reference
Isobutyraldehyde	118–119	125	17
α-Ethylbutyraldehyde	95–96	96	17
Methyl *n*-amyl ketone	123–124	121–123	18
Di-*n*-butyl ketone	90–91	90	19
Pinacolone	157–158	157	20

hyde (7%). The concentrations of the semicarbazone solutions were as follows: isobutyraldehyde 20%, α-ethylbutyraldehyde 15%, methyl *n*-amyl ketone 7%, di-*n*-butyl ketone 14%, pinacolone 10%.

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(11) H. Brunner and E. H. Farmer, *J. Chem. Soc.*, 1039 (1937).

(12) F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **75**, 6026 (1953).

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(14) J. F. Bunnett, J. L. Marks, and H. Moe, *J. Am. Chem. Soc.*, **75**, 985 (1953).

(15) H. Adkins and A. G. Rossou, *J. Am. Chem. Soc.*, **71**, 3836 (1949).

(16) C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2955 (1930).

(17) Ref. (9), p. 283.

(18) W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 99 (1940).

(19) Ref. (9), p. 316.

(20) A. Michael, *J. Am. Chem. Soc.*, **41**, 417 (1919).

[Contribution from the Department of Chemistry, Canisius College]

Abnormal Beckmann Rearrangements in Polyphosphoric Acid. I. Benzil Monoxime and Related Oximes[1,2]

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Received August 15, 1958

The Beckmann rearrangement of alpha-benzil monoxime and alpha-benzoin oxime in polyphosphoric acid to yield benzonitrile as one of the rearrangement products in each case is reported. These data, together with the direct nitrosation of desoxybenzoin, indicate the rearrangements of these oximes in polyphosphoric acid are examples of the abnormal Beckmann rearrangement rather than the normal Beckmann rearrangement as previously reported. The rearrangement of alpha-benzil dioxime in polyphosphoric acid quantitatively yields 3,5-diphenyl-1,2,4-oxadiazole.

The Beckmann rearrangement of alpha-benzil monoxime and alpha-benzoin oxime has been the subject of extensive study.[4] Although the nature of the products has varied with the acid catalyst used and the conditions of the reaction, in general, each oxime has been shown to yield products which could arise from an initial normal Beckmann rearrangement.[5] It has been reported,[6] that alpha-benzil monoxime (I) in polyphosphoric acid at 120° undergoes the Beckmann transformation to yield initially dibenzamide (II) as shown in Fig. 1. The dibenzamide was believed to be hydrolyzed by the medium to yield the isolated products, namely, benzoic acid and benzamide. These

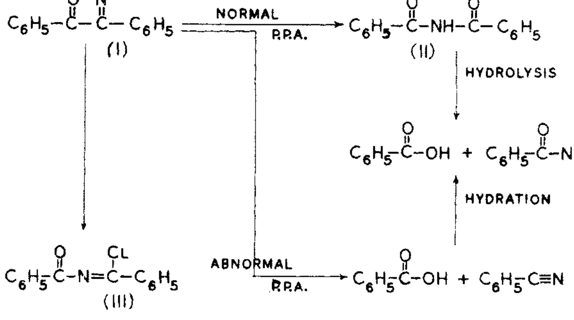

Figure 1

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(1) Preliminary results of this investigation are reported in *Tetrahedron*, **3**, 90 (1958).

(2) This work was supported by a Frederick Gardner Cottrell grant from the Research Corp.

(3) Abstracted in part from the thesis submitted by F. A Mikulski to the Department of Chemistry, Canisius College in fulfillment of the requirements for the Bachelor of Science degree.

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(5) N. V. Sidgwick, *The Organic Chemistry of Nitrogen*, (revised and rewritten by T. W. J. Taylor and W. Baker), Oxford University Press, 1942, p. 182.

(6) E. C. Horning, V. L. Stromberg, and H. A. Lloyd, *J. Am. Chem. Soc.*, **74**, 5153 (1952).