The various organic substances listed in Table III do not interfere. However, large negative errors were found in the absence of bromide, as shown in Table III. Only with ethyl acetate were fairly satisfactory results obtained in the absence of bromide.

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Formation, Separation, and Identification of the 2,4-Dinitrophenylhydrazones

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This work was conducted to explain and evaluate some of the conflicting data reported in the literature on the 2,4-dinitrophenylhydrazones. Various analytical techniques have been applied to the study of the use of 2,4-dinitrophenylhydrazine as a reagent for carbonyl compounds. It is concluded that the discrepancies found in the literature may be due to the occurrence of geometrical isomerism, polymorphism, mixed-crystal formation, structural rearrangements, or side reactions.

IT HAS been shown that the discrepancies in the literature concerning the physical properties of the 2,4-dinitrophenylhydrazones may arise from several sources: geometrical isomerism (*8–10, 12, 21, 23, 25, 36*), polymorphism (*3, 13, 14, 18, 22, 31*), formation of mixed crystals (*6*), rearrangements (*1, 5*), and side reactions (*16, 19, 27, 28, 37*). Further studies were found to be in agreement with this. The results are presented in this paper.

The most outstanding example of isomerism is in the work of Brederick (*8, 9*), who reported two forms of furfural 2,4-dinitrophenylhydrazone melting at 212–214° and 230° C., respectively, with a mixed melting point of 185° C. It has been possible not only to reproduce his work, but also to separate the two forms on a chromatographic column using a bentonite–silica gel mixture as absorbent, and to differentiate between them by means of spectrophotometric, optical-crystallographic, and x-ray diffraction data (Figure 1, Tables I and II).

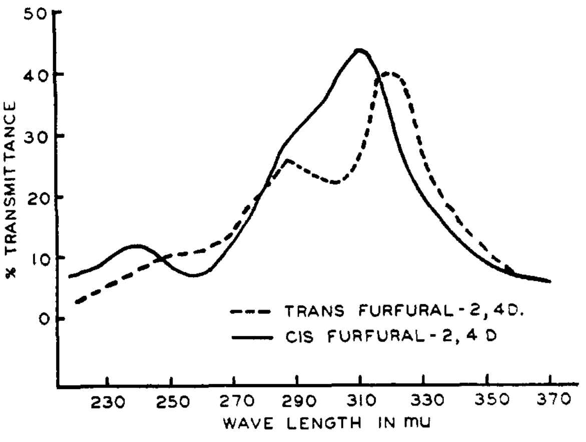


Figure 1. Ultraviolet Absorption of Furfural 2,4-Dinitrophenylhydrazones

Concentration, 20 mg. per liter
Cell length, 1 cm.

To determine the effect of polymorphism on the melting point of a derivative in the presence of foreign impurities, a phase study was made of the binary system acetone and diisobutyl ketone 2,4-dinitrophenylhydrazones (Figure 2). Acetone 2,4-dinitrophenylhydrazone is dimorphic, with a transition temperature of 124° C. The high-temperature form exists metastably below the transition point, forming a eutectic mixture (melting

Table I. Optical Properties of Furfural 2,4-Dinitrophenylhydrazone

Derivative	cis-Derivative	trans-Derivative
Melting point, ° C.	210	229
Crystal system	Orthorhombic	Monoclinic
Form and habit	Thin laminated plates, prismatic	Tabular, with ortho- and clinopinacoids
Interfacial	....	78° (silhouette)
Optic sign	Positive	Negative
Orientation	$a = Z$	$b = X$, $Y \wedge c = 25°$ Optic plane normal to 010
Pleochroism	Y yellow X orange	Y light-orange Z dark-red

Table II. Principal X-Ray Powder Diffraction Lines

cis-Derivative		trans-Derivative	
d, A.	I	d, A.	I
10.7	w	11.3	m
10.0	w	10.3	w
9.01	w	9.20	w
6.49	m	7.60	s
5.75	m	6.13	vs
4.86	m	4.43	s
4.34	s	3.82	m
3.93	s	3.24	s
3.73	s	3.22	s
3.45	m		
3.24	vs		

w, weak. m, medium. s, strong. vs, very strong.

point 76.3° C.) with the diisobutyl ketone derivative. This eutectic composition is 45 mole % acetone derivative. The eutectic with a composition of 35 mole % of the low-temperature form of acetone 2,4-dinitrophenylhydrazone melts at 80.1° C. Only one crystalline form of diisobutyl ketone 2,4-dinitrophenylhydrazone was found at the temperature of the experiment (70° to 130° C).

The 2,4-dinitrophenylhydrazones of formaldehyde, propionaldehyde, isobutyraldehyde, methyl ethyl ketone, and methyl *n*-amyl ketone also exhibit polymorphism.

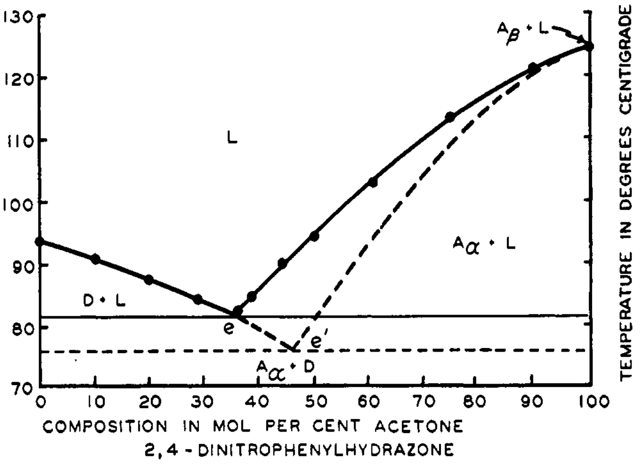


Figure 2. Phase Diagram of Binary System

2,4-Dinitrophenylhydrazones of acetone and diisobutyl ketone

The 2,4-dinitrophenylhydrazone of dipentadecyl ketone, prepared by the method of Shriner and Fuson (*35*), when purified to a constant melting point of 79° C., exhibited the optical properties of a pure compound. The Dumas nitrogen analysis, however, was 4.90% as compared with the calculated value of 8.36%. This discrepancy can be explained by assuming the existence of a mixed crystal of two molecules of ketone and one of the hydrazone, or of one molecule of ketone and one of its hydrazone. The derivatives of other high-weight ketones, such as dinonyl ketone and diheptadecyl ketone, behave in a similar manner.

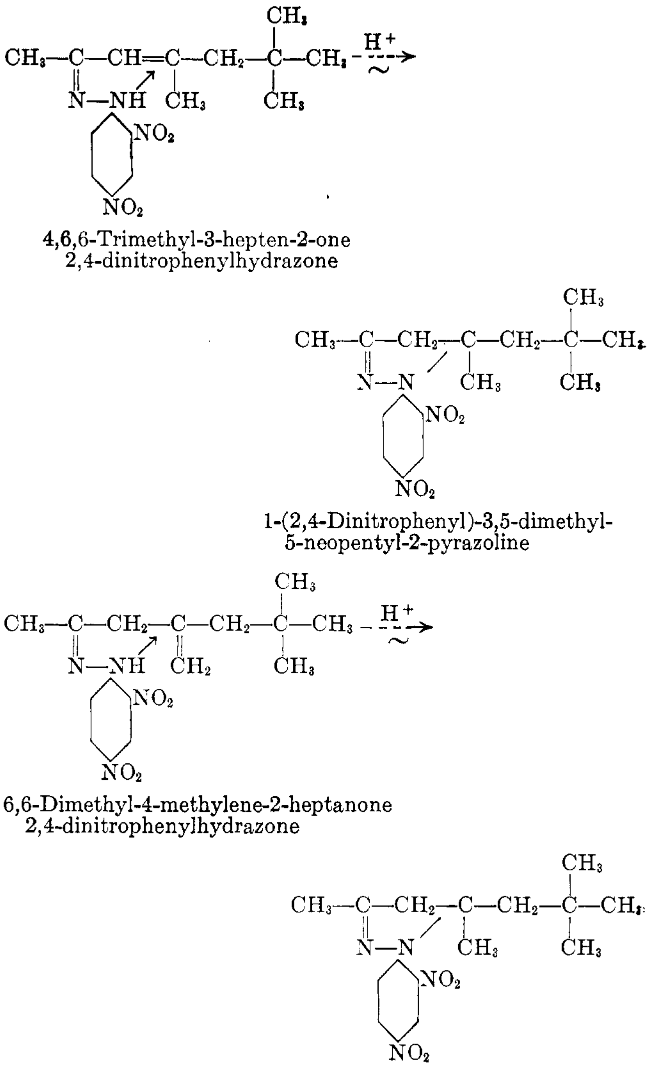
Rearrangements have been observed among the 2,4-dinitrophenylhydrazones of α,β-unsaturated carbonyl compounds. A rearrangement to a pyrazoline ring may explain the existence of two forms of dibenzalacetone 2,4-dinitrophenylhydrazone, one of which melts at 175° C. and the other at 205° C. The mixed melting point is 167° C. The 2,4-dinitrophenylhydrazones of the high- and low-boiling forms of 4,6,6-trimethyl-3-heptene-2-one and of the isomer 6,6-dimethyl-4-methylene-2-heptanone all melted at 166.5° C., possibly because of the formation of a pyrazoline ring as shown. At 0° C. it was possible to prepare a derivative of the low-boiling form of 4,6,6-trimethyl-3-heptene-2-one which melted at 137° C.

Because very few literature data could be found concerning the effect of varying reaction conditions on the formation of the 2,4-dinitrophenylhydrazones, the effect of changes in time, temperature, concentration, and acidity were investigated.

Variations in the temperature of the condensation were found to have very little effect upon the melting points of the 2,4-dinitrophenylhydrazones of most carbonyl compounds. Only in the case of the above-mentioned isomeric decenones and in that of acetaldehyde was any great difference noted. Although this may be due to impurities, when prepared at 0° C., the acetaldehyde 2,4-dinitrophenylhydrazone melts at 130° C.; when prepared at 20° C., it melts at 157° C.; and when prepared at 55° C., it melts at 145° C. However, for most routine work, room temperature seems to be entirely adequate, although cases requiring short periods of reflux do arise.

A study of the reaction acidity necessary to give best results was made using hydrochloric acid with both acetone and benzaldehyde. After standing for an hour, each sample was chromatographed on a 4 to 1 silica gel-bentonite mixture. Completion of the reaction was measured by the amount of unreacted reagent recovered. From Figure 3 it can be seen that an acidity concentration in the range of 1 ml. of concentrated hydrochloric acid per liter gives complete reaction under the conditions used.

The effect of the reaction time on yield was examined in the same manner. From Figure 4 it can be seen that although acetone reacted significantly more slowly than benzaldehyde, complete reaction was obtained in about half an hour.



4,6,6-Trimethyl-3-hepten-2-one 2,4-dinitrophenylhydrazone

1-(2,4-Dinitrophenyl)-3,5-dimethyl-5-neopentyl-2-pyrazoline

6,6-Dimethyl-4-methylene-2-heptanone 2,4-dinitrophenylhydrazone

1-(2,4-Dinitrophenyl)-3,5-dimethyl-5-neopentyl-2-pyrazoline

Possible Rearrangement of a Pyrazoline Ring

It was also found that an excess of either the hydrazine or the carbonyl compound, or even unreacted quantities of both, can be separated from the derivative by chromatographic methods.

While dissolving the commercial reagent in ether, it was noticed that a substantial residue was left which was insoluble in the solvent. By ether extraction of several different samples it was found that commercial 2,4-dinitrophenylhydrazine contains about 2.43% potassium sulfate. The inorganic salt had no

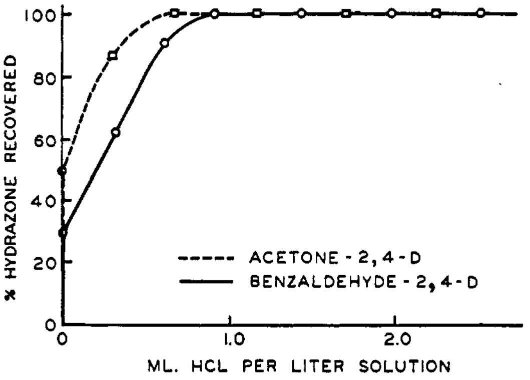


Figure 3. Influence of Acidity on Reaction Completion

effect on the melting point of the derivatives and could be detected microscopically. Ordinarily it is soluble in the reaction medium, and, if not, it can be filtered off at the start. If quantitative methods involving no recrystallization of the derivative are being used, the presence of this impurity must be kept in mind.

Chromatographic techniques occasionally indicated the presence of low-molecular-weight carbonyl compounds in the 95% ethyl alcohol frequently used as a solvent for the reaction. Distillation of the alcohol from solid alkali was sufficient to remove these compounds.

From the results of the above investigation and the literature references cited, it can be concluded that the nature and identity of the products of the condensation reaction cannot always be ensured by means of melting points alone. The two forms of furfural 2,4-dinitrophenylhydrazone were distinguished from each other by means of the spectrophotometer, the polarizing microscope, and the x-ray diffraction spectrometer. The literature offers some fine examples of the use of absorption spectra (*7, 20, 34, 38*), powder-diffraction patterns (*2, 14, 20, 23, 26, 30*), and optical-crystallographic data (*11, 32*) for the identification of 2,4-dinitrophenylhydrazones. Nothing concerning the polarographic determination of these compounds has appeared, however. Accordingly, the 2,4-dinitrophenylhydrazones of eight aldehydes of relatively low molecular weight were examined in this manner to ascertain the polarographic reducibility of the compounds, and the effect of changes in the parent carbonyl compound on the half-wave potential. The compounds studied produced a double wave in an acetone-water solution. The half-wave potentials were in the vicinity of -0.6 volt for the first wave and -0.9 volt for the second wave. The two waves were too close together for the diffusion current to be measured accurately on the instrument used, thus negating the value of the measurements for qualitative purposes. However, in the range of 5×10^{-5} to 4×10^{-4} M concentration, the diffusion current varies directly with the concentration, providing a means of quantitative analysis for these compounds.

In using 2,4-dinitrophenylhydrazine as an analytical tool, the analyst must be aware of the difficulties involved. These difficulties may be remedied by controlled reaction conditions, chromatographic purifications, and instrumental methods to ensure the identity, purity, and nature of the derivative.

EXPERIMENTAL

Isomers of Furfural 2,4-Dinitrophenylhydrazone. The isomers of furfural 2,4-dinitrophenylhydrazone were isolated by a modification of Brederick's method (*8, 9*) and chromatography.

PREPARATION AND ISOLATION. Ten grams of recrystallized Eastman Kodak White Label 2,4-dinitrophenylhydrazine (melting point 199° C.) was completely dissolved in 1.2 liters of boiling absolute ethyl alcohol containing 3 ml. of concentrated hydrochloric acid (specific gravity 1.188). The solution was allowed to cool for a few minutes, and then 5 ml. of furfural (boiling point 160° C./736 mm.; $n_D^{20} = 1.5260$) was added slowly with stirring. A light-red precipitate formed almost immediately, and the warm solution was decanted from this precipitate. Three successive recrystallizations of the residue from dioxane gave a crop of dark, purple-red, tabular crystals whose melting point was 229° C. The yellow form reported by Brederick was not observed.

As the solution cooled further, a voluminous orange-yellow precipitate appeared. Microscopic examination indicated the presence of a mixture of a red and a yellow form, melting at 185° C. Successive recrystallizations from dioxane and absolute ethyl alcohol gave a yellow crystalline product melting at 209° C. No red crystals were present.

A mixture of the two forms melted at 185° C.

Acetylation of each form with acetic anhydride and pyridine gave a product melting at 170° C. The mixed melting point of the acetylation products was 170° C. Hydrolysis of the acetylated product of each form yielded the red form of the furfural derivative in both cases, with melting points of 227° and 229° C.

These data are in agreement with the work reported by Brederick.

CHROMATOGRAPHIC TECHNIQUES. Preliminary experiments were run to determine the size of the column and type adsorbent to use. It was finally decided to use a glass column measuring 20 × 400 mm. The adsorbent chosen was a 4 to 1 mixture of silica gel (150- to 200-mesh) and bentonite (80- to 100-mesh).

A reagent solution containing 1 gram of 2,4-dinitrophenylhydrazine in 1 liter of anhydrous ether was prepared. To this was added 1 ml. of concentrated hydrochloric acid.

Two drops of furfural were added to 10 ml. of the reagent solution. After standing for half an hour, the reaction solution was added to the packed column, and eluted with 100 ml. of anhydrous ether under pressure. The development of an orange band below the limit of the first adsorption began immediately. Elution was continued until this band was washed off. The column was then extruded and the red band removed with an acetone-ether mixture. Evaporation of the ether solution gave yellow, orthorhombic plates melting at 210° C. Red, monoclinic, tabular crystals which melted at 229° C. were obtained from the acetone-ether solution. The yellow form was found to be identical with Brederick's cis-form by comparison using a polarizing microscope. The red form was similarly identified as the trans-form of Brederick.

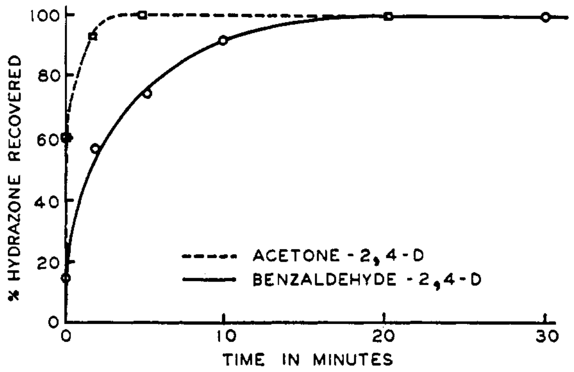


Figure 4. Influence of Time on Reaction Completion

Binary System: Acetone and Diisobutyl Ketone 2,4-Dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazones were prepared by Brady's method (*4*), and purified by recrystallization from ethyl alcohol and ligroine.

Heating curves were obtained from an apparatus similar to that of Lynn (*29*), the chief modification being an additional jacket containing glycerol for better control of the rate of heating. With these curves, eutectic temperatures could be determined accurately; the point of complete melting, however, was indefinite, and had to be determined with an electrically heated melting point block similar to that described by Morton (*33*).

The behavior of the system was checked with a polarizing microscope equipped with a micro hot stage (*24*).

Table III. Optical Crystallographic Properties of 2,4-Dinitrophenylhydrazones

Derivative of	Crystal System	Form	Orientation	Optic Sign	$2E$	Dispersion	Transmittance
Formaldehyde							
From 95% ethyl alcohol	Monoclinic	Orange prisms	$OAP = 010$ $X \wedge c = 37° \pm 1°$ $Y = b$	Negative	130° (5461 A.) 130° (5769-91 A.)	None observed	X 5075-6700 A. Y 5100-6700 A. Z 5000-6700 A.
From fusion				Negative	86° (5461 A.) 92° (5769-91 A.)	Axial	X 5000-6800 A. Y 5200-6600 A. Z 5100-6800 A.
Propionaldehyde							
From 95% ethyl alcohol	Monoclinic	Red-orange prisms	Below 6240 A, $OAP = 010$ Above 6240 A, $OAP \perp 010$ $X \wedge c = 38° \perp 1°$	Negative	48° (5351 A.) 21° (5893 A.) 40° (5461 A.) 1° (6234 A.) 26° (5780 A.) 0° (6240 A.) 17° (6808 A.)	Crossed-axial plane (6240 A.)	X 5150-6500 A. Y 5300-6800 A. Z 5350-6800 A.
From fusion	Orthorhombic	Prisms	$OAP = 100$, $X = b$ $Y = a$, $Z = c$	Negative	49° (5461 A.) 57° (5769-91 A.)	Axial	X 5200-6600 A. Y 5400-6800 A. Z 5350-6800 A.
Isobutyraldehyde							
From 95% ethyl alcohol	Hexagonal	Elongated yellow prisms		Negative			E 5050-6500 A. O 5200-6500 A.
From fusion	Orthorhombic	Prisms	$OAP = 010$, $X = a$ $Y = b$, $Z = c$	Negative	86° (5461 A.) 90° (5769-91 A.)	Axial	X 5000-6600 A. Y 5200-6600 A. Z 5300-6600 A.
Methyl ethyl ketone							
From 95% ethyl alcohol	Monoclinic	Elongated, light-orange prisms	$OAP = 010$ $X \wedge c = 3-5°$	Negative	Not determined, for figure is rather diffuse		X 5100-6500 A. Z 5200-6500 A.
From fusion I	Monoclinic		$OAP = 010$ $Z \wedge c = 2-3°$	Negative	70° (5461 A.) 98° (5769-91 A.)	Slight, inclined	Y 5250-6500 A. Z 5100-6500 A.
From fusion II	Monoclinic			Negative	40° (5461 A.) 82° (5769-91 A.)	Axial	Y 5400-6700 A. Z 5200-5300 A. and 5400-6600 A., Z shows adsorption band from 5300-5400 A.
Methyl n-amyl ketone							
From 95% ethyl alcohol	Orthorhombic	Very small, light-orange, elongated prisms	$OAP = 100$ $X = c$ $Z = b$	Negative	124° (4561 A. and 5769 A.)	None observed	X 4600-7000 A. Z 5200-6900 A.
From fusion	Orthorhombic	Prisms	$OAP = 010$ $Z = c$ $X = a$	Negative	32° (5461 A.) 33° (5769-91 A.)	Axial	X 4900-6800 A. Y 5300-6900 A. Z 5300-6800 A.

Polymorphism of Various 2,4-Dinitrophenylhydrazones. The carbonyl compounds investigated were: formaldehyde (Baker's U.S.P. formalin solution), propionaldehyde (boiling point 48.5° C./738 mm.; $n_D^{20} = 1.3637$), isobutyraldehyde (boiling point 61° C./740 mm.; $n_D^{20} = 1.3730$), methyl ethyl ketone (boiling point 79° C./738 mm.; $n_D^{20} = 1.3786$) and methyl n-amyl ketone (boiling point 150° C./740 mm.; $n_D^{20} = 1.4084$).

A Bausch and Lomb L. C. petrographic microscope, a Bausch and Lomb modified Emmons-Federof five-circle universal stage, and a Zeiss microspectroscope were used to obtain the data given in Table III.

The assignment of the crystals to a probable crystal system is based on the symmetry of the crystals as they appear when observed with a microscope. For accurate designations of the system, goniometer measurements are necessary. In designating the faces present and the orientation, it is assumed that the longest dimension of the crystal is the crystallographic axis c, the medium dimension b, and the shortest a, when these relative values are consistent with the crystal symmetry.

Mixed-Crystal Formation. The reaction was run in essentially the manner recommended by Brady (*4*). The dipentadecyl ketone (melting 82–84° C.) was furnished by H. D. Zook of the Pennsylvania State College. The reaction was refluxed for 20 minutes.

PHYSICAL PROPERTIES. Crude yield. 85%
  Crude melting point. 77–79° C. (On occasions a constant-melting mixture at 53° C. could be obtained when crude material was recrystallized from ethyl alcohol, but one recrystallization from ligroine would raise melting point to 78° C.)
  Color. Yellow
  Melting point from methanol. 78–79° C.
  Melting point from nitromethane. 78–79° C.
  Mixed melting point with dipentadecyl ketone. 80° C.
  Transmittance maximum. 299 mμ
  Transmittance minimum. 367 mμ
CRYSTAL MORPHOLOGY. Crystal system. Monoclinic
  Forms. Tablets from ligroine or ethyl acetate lying on 010 face, elongated parallel to c axis, interfacial angle $100 \wedge 001 = 60°$
OPTICAL PROPERTIES. Refractive indices (25° C.). Alpha 1.52, beta 1.68, gamma 2.10
  Optical axial angle (25° C.). $2V$ = large
  Dispersion. Red greater than blue
  Optical axial plane. 010. $X \wedge c = 30°$
  Sign of double refraction. (+)
  Acute bisectrix. Z gamma
  Pleochroism. Yellow for vibrations parallel to X alpha. Red for vibrations parallel to Z gamma

Pyrazoline Ring Formation. The dibenzalacetone (melting point 112° C.) was prepared according to the material outlined by Conard and Dolliver (*15*).

The condensation was run by Brady's method. The red-crystalline product, examined for purity under a microscope, melted at 175° C. It was dissolved in the minimum amount of boiling glacial acetic acid and the solution allowed to reflux for 0.5 hour. After cooling overnight, a heavy crop of orange crystals appeared which, after filtration and drying, had a melting point of 205° C. Micro-Dumas nitrogen analyses were run:

Red crystals. N calcd. 13.4%, N found 13.2%
Orange crystals. N calcd. 13.4%, N found 13.3%

The mixed melting point of these two forms was 167° C. No polymorphism was noted during the heating of either form.

Three isomeric decanones were obtained from G. G. Ecke of The Pennsylvania State College:

6,6-Dimethyl-4-methylen-2-heptanone, boiling point 90° C./28 mm.; $n_D^{20} = 1.4389$
4,6,6-Trimethyl-3-hepten-2-one (low-boiling), boiling point 86° C./26 mm.; $n_D^{20} = 1.4509$
4,6,6-Trimethyl-3-hepten-2-one (high-boiling), boiling point 95° C./29 mm.; $n_D^{20} = 1.4554$

Attempts to prepare the 2,4-dinitrophenylhydrazones of these three compounds by Brady's method resulted in the same product in each case. It consisted of deep-red crystals with a melting point of 166–167° C., and the derivatives of the three ketones gave no mixed melting point depression with each other. Chromatographic absorption of the derivatives of each of the three compounds on a 4 to 1 silica gel–bentonite mixture gave only a single band in each case.

Effect of Temperature Variation. The 2,4-dinitrophenylhydrazones of benzaldehyde (188° C./726 mm.), crotonaldehyde (Eastman Kodak White Label), cinnamaldehyde (Eastman Kodak White Label), furfural (boiling point 160° C./726 mm.), diethyl ketone (boiling point 100–101° C./738 mm.), cyclohexanone (boiling point 154° C./736 mm.), acetophenone (Eastman Kodak White Label), benzophenone (Eastman Kodak White Label), benzil (melting point 99° C.), benzalacetone (melting point 41–42° C.), dibenzalacetone (melting point 112° C.), and the above-mentioned isomeric decanones were prepared by Brady's method (and by a modification using propylene glycol as a solvent) at 0°, 20°, and 55° C. The lower-temperature runs were made in an ice bath and a water bath. The high-temperature condensations were made in an electrically heated block of sheet aluminum large enough to hold a 50-ml. beaker. The only variations noted were in the preparation of the derivatives of acetaldehyde (0° C., melting point 130° C.; 20° C., melting point 157° C.; 55° C., melting point 166° C.), and of the lower-boiling form of 4,6,6-trimethyl-3-hepten-2-one (0° C., melting point 138° C.; 20° C., melting point 167° C.; 55° C., melting point 166° C.).

Effect of Reaction Acidity. A liter of dry ether containing 1.000 gram of reagent was divided into ten equal parts. To each of the ten portions, a different amount (0 to 9 drops, 1 drop = 0.03 ml.) of concentrated hydrochloric acid was added. Two 10-ml. samples were taken from each of the 100-ml. portions and to one of them was added 2 drops of acetone; to the other, 2 drops of benzaldehyde.

After the reaction mixture stood for 1 hour, each sample was chromatographed. Completion of the reaction was measured by the amount of unreacted reagent recovered. The adsorbent used was a 4 to 1 silica gel–bentonite mixture. Elution was done with anhydrous ether. The band or bands were washed off, collected in tared beakers, evaporated, and reweighed.

Figure 3 is a graph of the results. The theoretical yield of the acetone derivative was about 12 mg., and of the benzaldehyde derivative about 14 mg.

Effect of Reaction Time. Twenty-milliliter samples of the reagent mixture (containing 1.0000 gram of 2,4-dinitrophenylhydrazine and 1 ml. of concentrated hydrochloric acid made up to 1 liter with anhydrous ether) were pipetted into flasks fitted with corks. To ten flasks were added 2 drops of acetone, and to the remaining ten, 2 drops of benzaldehyde.

The samples were then chromatographed after different periods of time had elapsed. The adsorbent was 4 to 1 silica gel–bentonite mixture. Elution was done with anhydrous ether, and the band or bands were washed off, collected in tared beakers, evaporated, and reweighed.

The weights and melting points of the crystals collected are reported in Figure 4. The theoretical yield of the acetone derivative was about 12 mg., and of the benzaldehyde derivative, about 14 mg.

Effect of Reactant Excesses. A solution of benzophenone (melting point 48° C.) in anhydrous ether, a solution of its 2,4-dinitrophenylhydrazone (melting point 238° C.) in ether, and a solution of the reagent in ether were made up separately, each of the same concentration, 1 mg. per ml. Seven mixtures and three pure samples were run through a chromatographic column. The mixtures were made and chromatographed immediately, and no acid was added, so that a minimum of reaction would occur.

The weight of the compound or mixture added to the column in each case was 21 mg. The adsorbent was a 4 to 1 silica gel–bentonite mixture. Elution was done with anhydrous ether, and the band or bands were washed off, collected in tared beakers, evaporated, and reweighed.

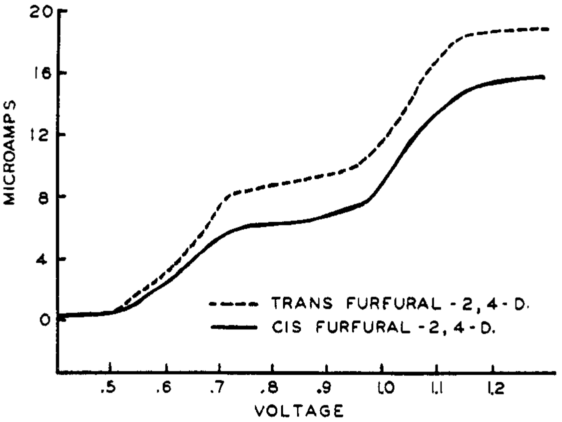


Figure 5. Polarographic Behavior of Furfural 2,4-Dinitrophenylhydrazone Stereoisomers

The results of the chromatographic separation of reactants and derivatives show: (1) Pure benzophenone, pure benzophenone 2,4-dinitrophenylhydrazone, and pure 2,4-dinitrophenylhydrazine were adsorbed individually and quantitatively, and when removed gave characteristic melting points. (2) Mixtures of benzophenone and benzophenone 2,4-dinitrophenylhydrazone were also separable and gave melting points of pure compounds, as did mixtures of the benzophenone 2,4-dinitrophenylhydrazone and the 2,4-dinitrophenylhydrazine. (3) Mixtures of benzophenone and the reagent or mixtures of all three did not give sharp separations or melting points characteristic of pure compounds.

Purity of Commercial 2,4-Dinitrophenylhydrazine. The amount of ether-insoluble residue in Eastman Kodak White Label 2,4-dinitrophenylhydrazine was estimated quantitatively by continuous ether extraction of several weighed samples. The samples were weighed into tared extraction thimbles which were placed in a Soxhlet apparatus and extracted until the ether wash was colorless. The thimble was then dried and reweighed. The gain in weight was reported as ether-insolubles. The thimbles had been previously washed to constant weight.

Two 2.0 ± 0.1 gram samples were taken from each of five new 50-gram bottles of 2,4-dinitrophenylhydrazine. The bottles were purchased from different sources, but all were originally made by the Eastman Kodak Co. The commercial reagent had

Table IV. Purification of 2,4-Dinitrophenylhydrazine

Sample	Wt. of Sample, Gram	Wt. of Residue, Gram	% Residue	Extraction Time, Days
1, Eastman	2.0009	0.0523	2.61	8
	2.0004	0.0490	2.45	9
2, E. & A.	1.9999	0.0392	1.96	11
	2.0012	0.0388	1.94	11
3, E. & A.	2.0000	0.0452	2.26	10
	2.0019	0.0508	2.53	10
4, Will	2.0002	0.0439	2.20	10
	1.9990	0.0471	2.25	10
5, will	1.9994	0.0509	2.54	10
	2.0011	0.0538	2.69	10

Table V. Polarographic Data of 2,4-Dinitrophenylhydrazones

Derivative of	Concn. $\times 10^{-5}$ *M*	First Wave		Second Wave		Total Wave	
		$-E^{1/2a}$	i_d	$-E^{1/2}$	i_d	$-E^{1/2}$	i_d
Ethanal	56.5	0.58	11.5	0.86	15.5	0.75	27.0
	28.2	0.60	8.62	0.83	8.75	0.70	17.37
	5.7	0.60	2.00	0.86	2.00	0.77	4.00
Propanal	16.8	0.63	3.40	0.87	2.85	0.54	6.25
	8.4	0.61	1.75	0.86	1.57	0.72	3.32
	5.6	0.56	1.15	0.83	1.15	0.65	2.30
2-Methylpropanal	19.4	0.67	5.91	1.05	4.50	0.90	10.41
	9.7	0.65	2.82	0.98	2.38	0.76	5.20
	1.9	0.60	1.20	0.90	0.60	0.63	1.80
Butanal	67.0	0.62	14.20	0.94	13.1	0.80	27.3
	12.8	0.62	4.2	0.92	3.0	0.68	7.2
	6.7	0.60	2.0	0.91	1.5	0.63	3.5
2,2,3-Trimethylbutanal	61.0	0.78	14.20	1.20	10.6	0.92	24.8
	12.2	0.69	2.60	1.01	3.4	0.92	6.0
	6.1	0.85	2.20	1.12	2.6	0.98	4.8
4-Methylpentanal	60.5	0.66	9.80	1.09	11.0	0.84	20.8
	12.1	0.61	2.40	0.92	2.30	0.80	4.7
	6.1	0.67	1.70	0.98	1.10	0.74	2.8
Hexanal	57.6	0.63	10.0	0.88	11.3	0.80	21.3
	28.8	0.58	5.5	0.87	6.1	0.80	11.6
	9.7	0.57	2.3	0.85	2.0	0.65	4.3

[a] $E^{1/2}$ is referred to standard calomel electrode.

a melting point of 199° C., and the recrystallization failed to raise this value significantly. The ether-insoluble residue was identified as potassium sulfate by means of qualitative tests and its optical-crystallographic properties.

Table IV gives the results.

POLAROGRAPHIC ANALYSIS

A polarographic analysis was run on the 2,4-dinitrophenylhydrazones of each of the following aldehydes: acetaldehyde, propanal, 2-methylpropanal, butanal, 2,2,3-trimethylbutanal, 4-methylpentanal, *n*-hexanal, and furfural. The derivatives were prepared by Brady's method. The modification of the acetaldehyde derivative used melted at 168° C. Both forms of furfural 2,4-dinitrophenylhydrazone were used.

The acetone-water buffer of Cray and Westrip (*17*) with a pH of 9.45 was used as a solvent. All measurements were made on an Aminco polarometric analyzer No. 5-2500. The curves were analogous to those reproduced for the furfural derivatives (Figure 5).

In Table V, $E^{1/2}$ designates the half-wave potential and i_d the diffusion current in microamperes. Concentration is given in moles per liter. The "total wave" was measured from the residual current to the upper limiting current.

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X-Ray Investigation of Several Contaminated Barium Sulfate Precipitates

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IN RECENT years much progress has been made in understanding the mechanism by which coprecipitation occurs during the formation of barium sulfate precipitates. The adsorptive properties of freshly precipitated barium sulfate for foreign ions have been investigated by Weiser and Sherrick (*13*) and by Nichols and Smith (*8*). Cohen's method (*6, 11*) for the determination of precise lattice constants from x-ray diffraction patterns has enabled Walden and coworkers (*2, 11, 12*) to demonstrate the importance of solid solution in accounting for the contamination of barium sulfate precipitates by nitrate, permanganate, water, and several univalent cations.

The x-ray diffraction technique has been applied here to investigate the nature of contamination of barium sulfate precipitates by ferric, chloride, and nitrite ions, all of which have been reported (*10*) to be strongly coprecipitated during the formation of barium sulfate.

PREPARATION OF PRECIPITATES

Barium sulfate precipitates were prepared in a manner which excluded all contamination except water and the contaminating ion under study. Reagent grade chemicals were used throughout.

"Pure" barium sulfate was precipitated by adding 50 ml. of approximately 0.2 *M* carbonate-free barium hydroxide dropwise to 200 ml. of a boiling, mechanically stirred, approximately 0.1 *M* sulfuric acid solution. The precipitates were digested in the hot solution for 4 hours and washed by decantation with 2 liters of hot water. They were then filtered through sintered-glass funnels, rewashed, and oven-dried for 2 hours at 130° C. This procedure was also employed to prepare all the contaminated precipitates except for the changes noted below.

Ferric ion contamination was introduced by adding ferric sulfate to the sulfuric acid before precipitation; the sulfate ion concentration was maintained constant by dilution with sulfuric acid while the ferric ion concentration was varied from 0.025 to 1.0 *M*. These precipitates were washed with dilute acid to prevent subsequent precipitation of ferric hydroxide on the surface of the barium sulfate. The pH of the mixed solutions was less than 2.

Chloride-contaminated precipitates were prepared by adding hydrochloric acid in varying amounts to each of the precipitating solutions. Chloride content, 0.5 to 3.0 *M*, was adjusted so as to be equal in both solutions before mixing.

The instability of nitrous acid made it necessary to premix