The Use of 2:4-Dinitrophenylhydrazine as a Reagent for Carbonyl Compounds

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WHILE employing 2:4-dinitrophenylhydrazine for the characterisation and identification of aldehydes and ketones, it was observed that there were a considerable number of discrepancies in the recorded melting-points. Analysts referring to older tables will also find discrepancies between these and more recent papers. It was considered that a revision of many of these melting-points and a tabulated comparison of the recorded figures might clear the way to a more extended use of this valuable reagent. This has been done and certain hitherto unrecorded derivatives have been prepared and examined.

The 2:4-dinitrophenylhydrazine was prepared by the method of Brady,⁵ isopropyl alcohol being used in place of the more costly pure ethyl alcohol. The product was pure and did not require recrystallisation.

The dinitrophenylhydrazones were prepared as suggested by Brady,⁵ and certain experimental details may be of interest. It was found that the addition of dilute sulphuric acid was unnecessary, but that even when separation did not occur on cooling, boiling gently under reflux for from five to thirty minutes sufficed for condensation. Purified industrial methylated spirit was used as a substitute for ethyl alcohol, and in no instance did this cause complication. Recrystallisation was effected, whenever possible, from alcohol, but acetic acid was frequently found necessary, and when this solvent failed, xylene usually gave good results.

Two compounds not prepared by Brady's method were the dinitrophenylhydrazones of phenanthraquinone and chrysoquinone. These were obtained by boiling one mol. of the quinone with two mols. of dinitrophenylhydrazine in glacial acetic acid solution for thirty minutes. The crude substances did not require re-crystallisation.

Attention is drawn to the variations in the m.p. of the dinitrophenylhydrazone of acetaldehyde as recorded by various authors. These have been attributed by Bryant⁸ and others to the existence of a meta-stable form melting at 147° C. and a stable form melting at 168° C. It is true that the *crude* product obtained by Brady's method has m.p. 147° C., but I have been unable to confirm Bryant's statement that a meta-stable modification melting at this temperature is produced when the liquid phase is allowed to solidify. Indeed, no signs of such a meta-stable modification could be detected when the liquid was undercooled far below its m.p., in a narrow tube, and then inoculated with a crystal of the crude substance having m.p. 147° C. The so-called meta-stable form is undoubtedly merely impure substance, the impurity being probably crotonic aldehyde dinitrophenylhydrazone, derived from some crotonic aldehyde produced from the acetaldehyde by the sulphuric acid used in Brady's method. Confirmation of this was obtained by the addition of excess of freshly distilled acetaldehyde to a cold pyridine solution of dinitrophenylhydrazine. Under these conditions the formation of crotonic

TABLE I

2:4-DINITROPHENYLHYDRAZINE DERIVATIVES OF ALDEHYDES

Aldehyde	Solvent	Colour	Melting- point °C.	Recorded melting-points
Formaldehyde	. Alcohol	Yellow	166°	(1) 155°, (4) 155°, (6) 167°
Acetaldehyde	. Alcohol	Orange- yellow	168°	(1) 147°, (4) 147°, (6) 167°
Propionaldehyde	. Alcohol	Orange	154°	(3) 155°, (4) 155°, (6) 156°
n-Heptylaldehyde (Oenanthol) Alcohol	Yellow	108°	(3) 106° , (4) 106°
Phenylacetaldehyde	. Alcohol	Yellow	121°	(5) 110°
Cinnamic aldehyde	. Acetic ac	id Red	255°	(5) 248°
Furfuraldehyde	. Xylene	Red	$(m decomp.) \ 229^\circ$	(1) 202°
Benzaldehyde	. Acetic ac	id Orange	237°	(1) 203° , (2) 235°
Salicylaldehyde	. Acetic ac	id Light red	252°	(1) 237° , (2) 248°
<i>m</i> -Hydroxybenzaldehyde .	. Alcohol	Red	(decomp.) 260° (decomp.)	(5) 259°
p-Hydroxybenzaldehyde .	. Acetic ac	id Purple-	280°	(1) 157°
o-Nitrobenzaldehyde	. Xylene	Yellow	(decomp.)	(1) 192°
<i>m</i> -Nitrobenzaldehyde	. Acetic ac	id Yellow	(decomp.) $292-293^{\circ}$ (decomp.)	(1) 268°
o-Chlorobenzaldehyde .	. Acetic ac	id Orange	206-207°	
Anisaldehyde	. Acetic ac	id Orange-	$253 - 254^{\circ}$	(5) 250°
Vanillin	. Acetic ac	id Red	271°	
Piperonal	. Acetic ac	id Red	(decomp.)	(5) 265°
Cumic aldehyde	. Acetic ac	id Red	(decomp.) 243°	(5) 241°
Citral	. Alcohol	Orange	116°	(4) $108-110^{\circ}a$, $96^{\circ}\beta$
Citronellal	. Alcohol	Yellow	77°	(4) 78°
n-Butyraldehyde*	•	Yellow		$(3) 122^{\circ}, (4) 122^{\circ}, (6) 123^{\circ}$
isoButyraldehyde	•	Yellow		(3) 182°, (4) 182°, (6) 187°
<i>n</i> -Valeraldehyde	•	Yellow		(4) 98°
isoValeraldehyde	•	Yellow		(3) 123°, (4) 123°
Trimethylacetaldehyde .		Yellow		(4) 210°
<i>n</i> -Caproic aldehyde		Yellow		(3) 104°, (4) 104°
<i>n</i> -Octyl aldehyde		Yellow		(4) 106°
<i>n</i> -Nonyl aldehyde		Yellow		(3) 96°, (4) 96°
<i>n</i> -Decyl aldehyde		Yellow		(4) 104°
<i>n</i> -Undecyl aldehyde	•	Yellow		(4) 104°
<i>n</i> -Duodecyl aldehyde .	•	Yellow		(4) 106°
Acrolein	•	Orange- red		(4) 165°
a -Methyl- β -ethyl acrolein .		Crimson		(4) 159°
p-Nitrobenzaldehyde		Orange		(5) 3 20°
2:4-Dinitrobenzaldehyde .		Yellow		(7) 258°
2:4:6-Trinitrobenzaldehyde.		Orange		(7) 208°

* The solvents, colours and melting-points of this and the following derivatives tabulated are recorded from the literature for convenience of reference.

TABLE II

2:4-DINITROPHENYLHYDRAZINE DERIVATIVES OF KETONES

Ketone		Solvent	Colour	Melting- point °C.	Recorded melting-points °C.
Methyl ethyl ketone		Alcohol	Orange	110–111°	(3) 115°
Acetone		Alcohol	Yellow	126°	(1) 118°, (2) 128°
Methyl propyl ketone	••	Alcohol	Orange- vellow	1 43–144 °	(4) 141°
cycloPentanone	••	Alcohol	Yellow	$146 - 147^{\circ}$	(4) 142°
cycloHexanone	••	Alcohol	Yellow	162°	(4) 160°
Diacetone alcohol		Alcohol	Light red	202–203°	
Benzylidene acetone	••	Acetic acid	Red	227°	(4) 223°
Dibenzylidene acetone	••	Acetic acid	Red	180°	
Cinnamylidene acetone	••	Acetic acid	Purple- red	$222-223^{\circ}$	
Dicinnamylidene acetone	••	Acetic acid	Red	208°	
Pyruvic acid	••	Alcohol	Yellow	218°	(4) 213°
Acetoacetic ester	••	Alcohol	Yellow	93–94°	(1) 95°, (2) 96°
Benzoylacetoacetic ester	• •	Acetic acid	Orange	222–22 3 °	
Mesityl oxide	••	Acetic acid	Red	203°	(4) 200°
Acetylacetone	••	Alcohol	Yellow	209°	
Diacetyl	••	Anisole	Orange	charred above 300°	
Acetophenone	••	Acetic acid	Orange- red	249–250°	(4) 237°
Benzylidene acetophenon	е	Acetic acid	Orange- red	(decomp.)	(4) 208
Cinnamylidene acetophen	one	Acetic acid	Red	$218-219^{\circ}$ (decomp.)	
β -Acetylnaphthalene	••	Acetic acid	Red	262° (decomp.)	
<i>l</i> -Carvone	••	Acetic acid	Red	193°	· (4) 189°
d-Carvone	••	Acetic acid	Red	190° J	
Menthone	••	Alcohol	Orange	146°	(4) 145°
Pulegone	••	Alcohol	Red	147°	(5) 142°
Piperitone	••	Alcohol	Red	119°	,
a-Ionone	••	Alcohol	Orange	150°	(5) coml. 125–128°
d-Camphor	••	Alcohol	Deep yellow	177°	(5) 175°
Benzophenone	••	Acetic acid	Orange	238-239°	(1) 229°
β -Benzoyinaphthalene	••	Acetic acid and alcohol	Orange- yellow	257–258°	
p-Benzoyldiphenyl	••	Acetic acid	Orange	214°	
Benzoin	••	Alcohol	Yellow	245°	(4) 234°
Furoin :.	••	Alcohol	Orange- red	216–217°	
Benzil	••	Alcohol	Yellow	189°	(1) 183–184°, (4) 185°
Phenanthraquinone	•••		Dark red	312-313°	
Chrysoquinone	••		Red- brown	(decomp.) 308–309° (decomp.)	

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	Melting-						
Ketone		Solvent	Colour	point °C.	Recorded melting-points °C.		
Methyl <i>n</i> -butyl ketone*			Orange-		(4) 106°		
Methyl n-amyl ketone	••		Orange- vellow		(4) 89°		
Methyl <i>n</i> -hexyl ketone	••		Orange		(4) 58°		
Methyl n-nonyl ketone	••		Yellow- orange		(4) 63°		
Methyl n-undecyl ketone	••		Yellow- orange		(4) 69°		
Methyl isopropyl ketone	••		Yellow- orange		(4) 117°		
Methyl isobutyl ketone	••		Orange- red		(4) 95°		
Methyl isoamyl ketone	••		Orange		(4) 95°		
Methyl isohexyl ketone	••		Orange- yellow		(4) 77°		
Methyl cyclohexyl ketone	••		Orange		(4) 140°		
Di-ethyl ketone	••		Pale		(4) 156°		
Ethyl n-propyl ketone	•••		Orange- vellow		(4) 130°		
Ethyl isobutyl ketone	••		Orange- yellow		(4) 75°		
Di- <i>n</i> -propyl ketone	••		Orange- yellow		(4) 75°		
cycloHeptanone	••	Alcohol	Orange- yellow		(5) 148°		
cycloOctanone	••	Alcohol	Orange- yellow		(5) 163°		
cycloPentadecanone	••	Alcohol	Yellow		(5) 105°		
Benzoyl acetone	••	Alcohol	Pale		(5) 151°		
Allyl acetone			Orange		(4) 104°		
Ethyl oxomalonate	••		Lemon		(4) 128°		
Levulinic acid			Yellow		(4) 92°		
Methyl benzoyl formate	••		Orange- yellow		(4) 171°		
Fenchone	••	Alcohol	Orange- yellow		(5) 140°		
Pinacolone	••		Orange- yellow		(4) 125°		
Methyl heptenone	••		Orange- red		(4) 81°		
a-Indanone	••		Orange- red		(4) 258°		
<i>n</i> -Butyroin	• •		Yellow		(4) 99°		
pseudoIonone	••		Deep red		(4) 143°		

TABLE II—continued

aldehyde is very improbable, and the crude product obtained by pouring the solution into water and then adding dilute hydrochloric acid had m.p. 164° C.

There is no difficulty in purifying the acetaldehyde dinitrophenylhydrazone prepared by Brady's method, provided that alcohol is used as a solvent, a single recrystallisation from this usually being sufficient. Benzene, xylene and similar solvents are less suitable, and, if used, often necessitate several re-crystallisations. The possibility of impurities being produced by the aldol condensation is, however, one which should be carefully borne in mind by analysts.

* The solvents, colours and melting-points of this and the following derivatives tabulated are recorded from the literature for convenience of reference.

SUMMARY.--(1) isoPropyl alcohol can be conveniently used in place of the more costly duty-paid pure ethyl alcohol in the preparation of 2:4-dinitrophenylhydrazine.

The melting-points of many dinitrophenylhydrazones recorded in the (2)Tables of corrected melting-points are given, and these literature are erroneous. tables include all melting-points given in the literature and also the melting-points of several hitherto undescribed dinitrophenylhydrazones.

The so-called meta-stable modification of acetaldehyde dinitrophenyl-(3)hydrazone is shown to be merely impure material.

(4) Attention is drawn to the possibility of an impure derivative being obtained, owing to the aldol condensation taking place when Brady's method of preparation is used.

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