

Preparation of 2,4 Dinitro-phenyl hydrazone (2,4-DNP) derivatives of aldehydes R-CHO / ketones R-Co-R

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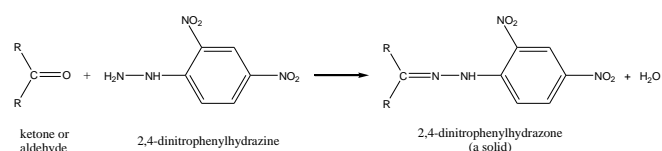
ABSTRACT

An alternative variation of the most common preparation of 2,4-dinitrophenylhydrazine reagent is presented. This method is suitable for scaling up for quantities required for preparing stock reagent for classes. Since the action of 2, 4-dinitrophenylhydrazine (Brady's reagent) on aldehydes and ketones was first investigated by Purgotti in 1894, its usefulness as an analytical reagent for carbonyl containing compounds has been thoroughly exploited. The 2, 4 -DNHP reagent is an orange crystalline solid melting at 199°C. Its usefulness as a reagent stems from the fact that it forms crystalline derivatives which are easily purified and have melting points supposedly characteristic of the aldehyde or ketone used in preparing the derivative. In principle, each aldehyde and ketone should form a single 2,4-dinitrophenylhydrazone (DNPH) with a characteristic melting point. In practice, however, a number of the aldehydes and ketones do not follow this general rule but form multiple derivatives, differing either in melting point, crystal structure, or both. Even the colors of pure DNPH's of a particular aldehyde or ketone are sometimes different.

Keywords : 2,4 DNP, Microwave, Aryl Aldehyde.

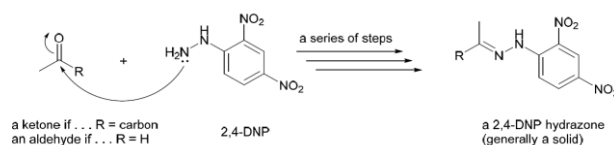
I. INTRODUCTION

2,4-Dinitrophenylhydrazine reacts with ketones and aldehydes, and is used to distinguish these functional groups from other carbonyl compounds, such as esters, which do not react. The formation of a red or orange precipitate (a 2,4-dinitrophenylhydrazone) constitutes a positive test.



Aldehydes and ketones react with 2,4-dinitrophenylhydrazine reagent to form yellow,

orange, or reddish-orange precipitates, whereas alcohols do not react. Formation of a precipitate therefore indicates the presence of an aldehyde or ketone. The precipitate from this test also serves as a solid derivative. A discussion on derivatives will be given later in this handout. The mechanism of this reaction is that of imine formation and can be found in any organic lecture text.



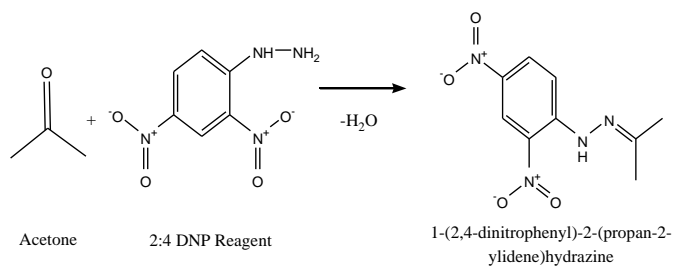
Crystals of the title compound, C₁₃H₁₀N₄O₄, were obtained from a condensation reaction of benzaldehyde and 2,4-dinitrophenylhydrazine. The molecule assumes an approximately

planar E configuration. Within the dinitrophenyl moiety, the average distance for the aromatic C-C bonds close to the imino group [1.417 (3) Å] is appreciably longer than the average distance for the other aromatic C-C bonds in the same phenyl ring [1.373 (3) Å]. This increased distance may be a result of the overlap of the non-bonding orbital of the imino N atom with the π orbitals of the arene. It is likely that π - π stacking exists in the crystal structure.

Principle :- 2,4 Dinitro-phenyl hydrazine reagent is much more reactive than phenyl hydrazine towards aldehydes and ketones. Both aldehydes and ketones contain a carbonyl group (-co-) of low reactivity often readily react with 2:4 DNP reagent to give a 2,4- dinitro-phenyl hydrazone derivative

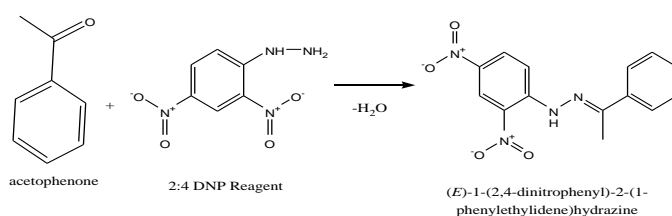
1. Synthesis of 1-(2,4-dinitrophenyl)-2-(propan-2-ylidene)hydrazine.

Take in a clean hard glass test tube 1 gm /ml of the acetone containing aldehyde/ ketonic group. Dissolve it in minimum amount of ethyl alcohol or methyl alcohol (if required heat on water bath). Cool the test tube and add 10 ml of 2:4 DNP reagent. Stir well with the help of glass rod and cool in ice bath. 2,4 dinitro-phenyl hydrazones usually separate in well-formed crystals. Filter it on Buchner funnel. Dry the crystal well and record the yield. Recrystallize 2,4 dinitro-phenyl hydrazone derivatives from ethyl alcohol. Dry the crystals well and find its melting point.



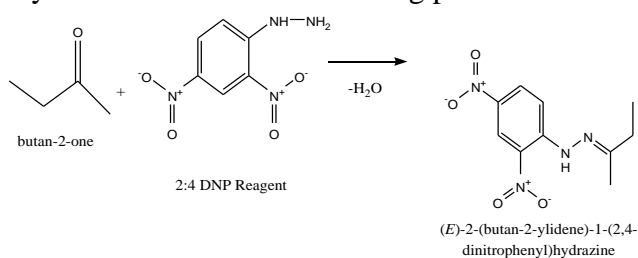
2. Synthesis of (E)-1-(2,4-dinitrophenyl)-2-(1-phenylethylidene)hydrazine

Take in a clean hard glass test tube 1 gm /ml of the acetophenone containing aldehyde/ ketonic group. Dissolve it in minimum amount of ethyl alcohol or methyl alcohol (if required heat on water bath). Cool the test tube and add 10 ml of 2:4 DNP reagent. Stir well with the help of glass rod and cool in ice bath. 2,4 dinitro-phenyl hydrazones usually separate in well-formed crystals. Filter it on Buchner funnel. Dry the crystal well and record the yield. Recrystallize 2,4 dinitro-phenyl hydrazone derivatives from ethyl alcohol. Dry the crystals well and find its melting point.



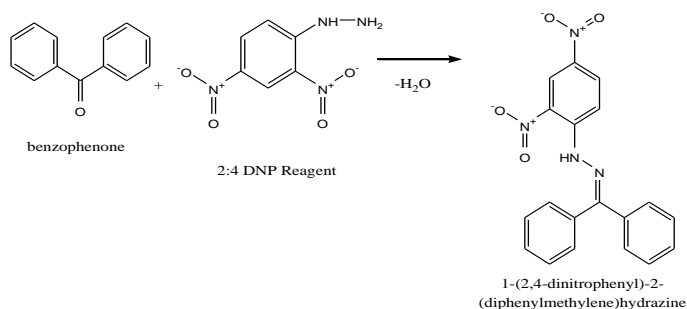
3. Synthesis of (E)-2-(butan-2-ylidene)-1-(2,4-dinitrophenyl)hydrazine.

Take in a clean hard glass test tube 1 gm /ml of the ethyl methyl ketone containing aldehyde/ ketonic group. Dissolve it in minimum amount of ethyl alcohol or methyl alcohol (if required heat on water bath). Cool the test tube and add 10 ml of 2:4 DNP reagent. Stir well with the help of glass rod and cool in ice bath. 2,4 dinitro-phenyl hydrazones usually separate in well-formed crystals. Filter it on Buchner funnel. Dry the crystal well and record the yield. Recrystallize 2,4 dinitro-phenyl hydrazone derivatives from ethyl alcohol. Dry the crystals well and find its melting point.



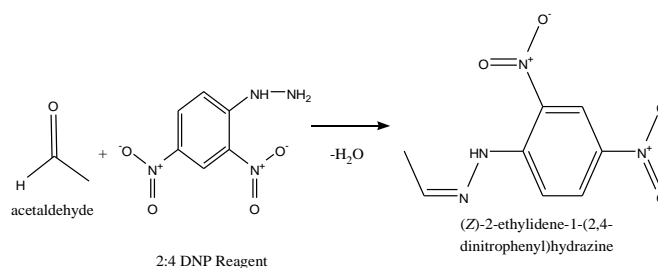
4. Synthesis of 1-(2,4-dinitrophenyl)-2-(diphenylmethylene)hydrazine.

Take in a clean hard glass test tube 1 gm /ml of the benzophenone containing aldehyde/ ketonic group. Dissolve it in minimum amount of ethyl alcohol or methyl alcohol (if required heat on water bath). Cool the test tube and add 10 ml of 2:4 DNP reagent. Stir well with the help of glass rod and cool in ice bath. 2,4 dinitro-phenyl hydrazones usually separate in well-formed crystals. Filter it on Buchner funnel. Dry the crystal well and record the yield. Recrystallize 2,4 dinitro-phenyl hydrazone derivatives from ethyl alcohol. Dry the crystals well and find its melting point.



5. Synthesis of (Z)-2-ethylidene-1-(2,4-dinitrophenyl)hydrazine

Take in a clean hard glass test tube 1 gm /ml of the acetaldehyde containing aldehyde/ ketonic group. Dissolve it in minimum amount of ethyl alcohol or methyl alcohol (if required heat on water bath). Cool the test tube and add 10 ml of 2:4 DNP reagent. Stir well with the help of glass rod and cool in ice bath. 2,4 dinitro-phenyl hydrazones usually separate in well-formed crystals. Filter it on Buchner funnel. Dry the crystal well and record the yield. Recrystallize 2,4 dinitro-phenyl hydrazone derivatives from ethyl alcohol. Dry the crystals well and find its melting point.



II. RESULTS AND DISCUSSION

Sr. No.	Compound Name	Molecular formula	Molecular Weight	M.P. °C	Yield %
01	1-(2,4-dinitrophenyl)-2-(propan-2-ylidene)hydrazine.	C ₉ H ₁₀ N ₄ O ₄	238	126 ⁰ C	82%
02	(E)-1-(2,4-dinitrophenyl)-2-(1-phenylethylidene)hydrazine.	C ₁₄ H ₁₂ N ₄ O ₄	300	146 ⁰ C	86%
03	(E)-2-(butan-2-ylidene)-1-(2,4-dinitrophenyl)hydrazine.	C ₁₀ H ₁₂ N ₄ O ₄	252	119 ⁰ C	80%
04	1-(2,4-dinitrophenyl)-2-(diphenylmethylene)hydrazine.	C ₁₉ H ₁₄ N ₄ O ₄	362	238 ⁰ C	76%
05	(Z)-2-ethylidene-1-(2,4-dinitrophenyl)hydrazine	C ₈ H ₈ N ₄ O ₄	224	165 ⁰ C	69%

- All the compound synthesized were adequately characterized by their spectral IR, ¹H-NMR & Mass Spectra.

*Spectral Study of 1-(2,4-dinitrophenyl)-2-(propan-2-ylidene)hydrazine:-

IR cm⁻¹ = 3305.64 (-NH), 1492.9(C=C), 1424.26(-NO₂)

^1H NMR:(δ ,ppm) (400MHz, DMSO) 2.1(d,3H), 2.0(dd,3H), 7.8(s, 1H), 8.3(s,1H), 8.9(s,1H), 10.8(1H,(exch.))(NH).

*Spectral Study of (E)-1-(2,4-dinitrophenyl)-2-(1-phenylethylidene)hydrazine

- ^1H NMR:(δ ,ppm) (400MHz, DMSO) 3.1(s,3H), 8.5(s,1H), 8.1(s,1H), 8.90(s,1H), 7.9(1H, (exch)(NH), 8.42(d,2H), 7.82(dd,2H), 7.5(d,1H).
- IR cm^{-1} = 3305.64 (-NH), 1498.70 (C=C), 1367.17(-NO₂)

*Spectral Study of (E)-2-(butan-2-ylidene)-1-(2,4-dinitrophenyl)hydrazine

- ^1H NMR:(δ ,ppm) (400MHz, DMSO) 2.1(t,3H), 2.5(q,2H), 3.3(s,3H), 10.0(1H(exch.)(NH), 7.8(s, 1H), 8.39(s,1H), 8.84(s,1H).
- IR cm^{-1} = 3384.95 (-NH),1605.69(C=C), 1490.60(-NO₂),1272.83(-C-C-)

*Spectral Study of 1-(2,4-dinitrophenyl)-2-(diphenylmethylene)hydrazine

- IR cm^{-1} = 3384.95 (-NH),1605.69(C=C), 1490.60(-NO₂),1272.83(-C-C-)

*Spectral Study of (Z)-2-ethylidene-1-(2,4-dinitrophenyl)hydrazine

- IR cm^{-1} = 3384.95 (-NH),1605.69(C=C), 1490.60(-NO₂),1272.83(-C-C-)

III. CONCLUSION

1. 2,4 Dinitrophenyl hydrazine can be used to qualitatively detect the carbonyl functionality of a ketone or aldehyde functional group.
2. If the carbonyl compound aromatic then the precipitate will be red.
3. If aliphatic, then the precipitate will have a more yellow colour.
4. The "DNP" test is positive for both aldehydes or ketones, But not for alkenes or ester / acids / amids.

5. This is representative of how H₂N-Z reagents react with aldehydes or ketones to eliminate water and make "imines" with a C=N-Z bond. In the chemical test, the DNP reagent is soluble, if a derivative forms, it precipitates from solution.
6. The DNP-derivatives tend to be highly crystalline.
7. The colour of the precipitate is often informative, saturated carbonyl compounds tend to give yellow derivatives, while unsaturated aldehydes or ketones tend to give red or orange derivatives

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V. REFERENCES

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