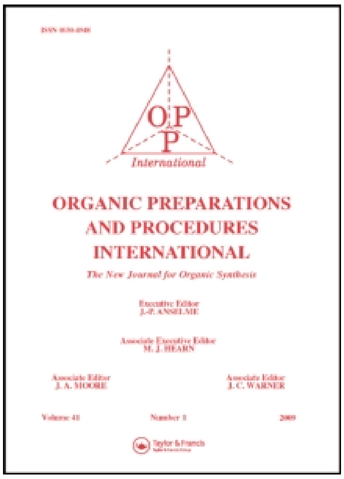

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ANHYDRIDE ACYLATION REACTIONS OF 2,4-DINITROPHENYLHYDRAZINE

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ANHYDRIDE ACYLATION REACTIONS OF 2,4-DINITROPHENYLHYDRAZINE

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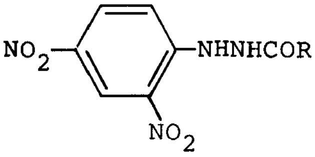
A convenient high yield preparation of 1-acyl-2-phenylhydrazines under mild conditions was recently described,[1] and we now report on the formation of the related 1-acyl-2-(2,4-dinitro)phenylhydrazines and comment on the substantive differences observed in synthesis and physical and spectral properties. Although some members of this class of carboxylic acid derivatives are known, general methods for their inexpensive preparation on useful scale from the anhydrides, as well as certain details of their characterization, have been neglected.[2-5]

In sharp contrast to the unsubstituted parent compound, 2,4-dinitrophenylhydrazine required a polar solvent and reflux temperature in order to undergo acylation with anhydrides. Thus 2,4-dinitrophenylhydrazine (18.5 mmoles) as a heterogeneous mixture in boiling 95% ethanol (40 ml) reacted smoothly with aliphatic anhydrides (40 mmoles) to yield the acylated products I (Table 1). The 1-acyl-2-(2,4-dinitro)phenylhydradines have considerably higher mps than those of their unsubstituted counterparts, and are less soluble in common organic solvents. The nmr spectra display the characteristic pattern of signals corresponding to 1,2,4-substitution on the electron-poor aromatic ring. The carbonyl peaks in the IR spectra show a substantial bathochromic shift (ca. 20 cm^{-1}) compared to those of the unsubstituted hydrazines. Though the presence of the nitro groups precludes reaction of the 2,4-dinitrophenylhydrazine with isatoic anhydride, phenylhydrazine itself reacts readily to yield the phenylhydrazide of anthranilic acid.[6] These results suggest the potent influ-



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a) R = CH_3 c) R = $CH_3CH_2CH_2$

b) R = CH_3CH_2 d) R = $(CH_3)_2CH$

TABLE. 1-Acyl-2-(2,4-dinitro)phenylhydrazines

Compound	mp (°C)	CO (cm^{-1})	% Yield
Ia	201 (129)[a]	1610 (1630)	64
Ib	192 (157)	1615 (1630)	67
Ic	157-158 (95-96)	1600 (1630)	57
Id	214-215 (139-140)	1600 (1630)	40[b]

[a] Numbers in parentheses refer to the mp of the corresponding 1-acyl-2-phenylhydrazine, prepared as noted in ref. 1.

[b] Molar ratio of anhydride to hydrazine in this case 26:20; cf. representative procedure below.

ence which even remote substituents may have on the reactivity of arylhydrazines and on the properties of the resultant products.[7]

EXPERIMENTAL SECTION

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Melting points were taken in open capillary tubes using a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 727 spectrophotometer as Nujol mulls. Nmr spectra were obtained on a Perkin-Elmer R-32 90 Mc spectrometer in acetone-d6 with tetramethylsilane as the internal standard. 2,4-Dinitrophenylhydrazine and carboxylic acid anhydrides were used as received from Aldrich Chemical Company or Eastman Company.

1-Acyl-2-(2,4-dinitro)phenylhydrazines. *Representative Procedure*.- To a heterogeneous mixture of 2,4-dinitrophenylhydrazine (3.67 g, 18.5 mmoles) in refluxing 95% ethanol (40 ml) was added dropwise acetic anhydride (4.08 g, 40 mmoles) over a period of about 10 minutes. The addition of the anhydride caused the mixture to boil all the more rapidly and to undergo a distinct change in color from red to a darker orange-red. After 30 minutes, all of the remaining solid had dissolved. Boiling was continued for a total of 1 hr, the mixture was removed and chilled in an ice bath; almost instantly yellow crystals precipitated and crystallization was complete after 15 min. 1-Acetyl-2-(2,4-dinitro)phenylhydrazine (Ia, 2.84 g, 64%) was recrystallized from 95% ethanol and obtained as unusually long yellow needles, mp. 201°, lit.[2] mp. $197-198^{\circ}$. IR 3328, 3155, 1651 cm^{-1}; NMR: δ 9.0 (broad s, 1H), 8.4 (d, 1H, J = 9 cps), 7.5 (d, 1H, J = 9 cps), 2.2 (s, 3H). A further portion of less pure material (1.28 g, 29%) was obtained

Anal. Calcd. for $C_8H_8N_4O_5$: C, 40.01; H, 3.36; N, 23.33.

Found: C, 39.86; H, 3.36, N, 23.17.

by evaporation of the mother liquor.

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NEW PREPARATION OF N-METHYLIMIDAZOLE-4,5-DICARBOXALDEHYDES AND SOME OF ITS REACTIONS

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(4/27/82)

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In the context of our interest in imidazoles,[1] we now report a new method for the preparation of N-methylimidazole-4,5-dicarboxaldehyde (III) from 4,5-diiodo-N-methylimidazole (I) in very good yield. This compound was previously pre-