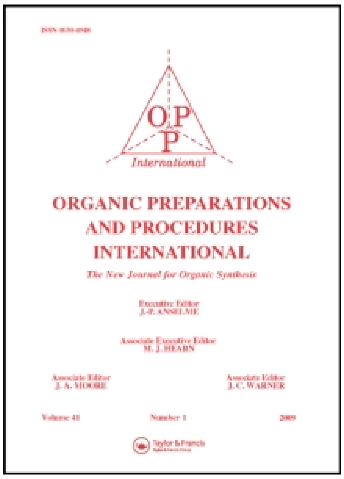

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IMPROVED SYNTHESES OF PICRYLHYDRAZINE AND OF THE PICRYLHYDRAZONES OF ACETONE AND OF ACETALDEHYDE

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IMPROVED SYNTHESES OF PICRYLHYDRAZINE AND OF THE PICRYLHYDRAZONES OF ACETONE AND OF ACETALDEHYDE

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The preparation of acetone and of acetaldehyde 2,4,6-trinitrophenylhydrazones (I and II) were reported some time ago.[1,2] Somewhat more recently, a procedure has been described for the preparation of the corresponding arylhydrazine (III).[3] These methods, in our hands and as used by others,[4] result in very poor yields (<5%).

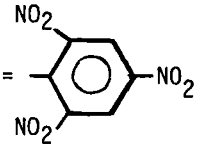
$(CH_3)_2C{=}NNHAr$

I

$CH_3CH{=}NNHAr$

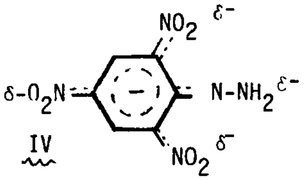
II

Ar– =



$ArNHNH_2$

III



IV

We have succeeded in improving the yields of arylhydrazine III, by use of the aprotic solvent glyme (1,2-dimethoxyethane) for the reaction of hydrazine hydrate with picryl chloride. Use of hydroxylic solvents invariably has lead to substantially lower yields, both in our laboratories and elsewhere.[3,4]

The formation of hydrazone I and II from this arylhydrazine was surprisingly facile. Although the formation of the corresponding

2,4-dinitrophenyl-, p-nitrophenyl- and phenylhydrazones all require added acid for catalysis[5], the preparations of **I** and **II** did not require such added acid. Indeed, our early attempts at recrystallization of the trinitrophenylhydrazine from acetone resulted in substantial amounts of **I**. One could speculate that the reaction is facilitated by (acid) autocatalysis; the proton availability would likely be promoted by the stabilized anion (**IV**). Our yields (90%) and purity (mp. 130-133°) of **I** were high only when nitrogen purged solvents were used for recrystallization. Preparation of **II** was achieved with comparable success. *It is critical that that nitrogen purged solvents and aprotic solvents be used throughout this procedure*. The high yield of arylhydrazines and arylhydrazones by our procedures is very possibly due to the lack of competitive reactions (e.g. Meisenheimer complexes form readily in alcohol[6]).

EXPERIMENTAL

*2,4,6-Trinitrophenylhydrazine (Picryl Hydrazine, **III**)*. - To a stirred solution of 10.2 grams (41 mmol.) of 2,4,6-trinitrophenyl chloride, mp. 180-184°, (Eastman 827) in 800 ml of dried 1,2-dimethoxyethane (Eastman 4639) was slowly added, dropwise, a solution of 2.4 ml. (41 mmol.) of hydrazine hydrate (technical, 85%, Matheson, Coleman, and Bell, T 5070) in 200 ml. of 1,2-dimethoxyethane (Glyme). The reaction was carried out, with stirring, in a 2 l., 3-necked, round bottom flask cooled in an ice bath. As each drop of hydrazine hydrate solution entered the yellow solution, a reddish-brown spot appeared which quickly dissipated. Eventually, the entire solution became red-brown (excess hydrazine hydrate would result in a deep purple solution). No heat evolution or gas bubbles were observed. After stirring at room temperature for 12 hours, the solution was filtered to remove unreacted starting material and then evaporated *in vauco at room temperature* leaving a red-brown solid (mp.

100-140°, typically 40% starting material by NMR). This solid product was purified by washing with cold, *nitrogen purged* ethanol or chloroform. After one washing with chloroform, 2.0 g. of a bright red-brown solid was obtained, mp. 180-184°, lit.[2,3] mp. 175-186°, 40% net yield. Slightly higher yields (54% net) were obtained when the glassware was modified to accomodate a flow of nitrogen and a dry-ice/acetone bath.

The infrared and proton magnetic resonance absorptions of this 2,4,6-trinitrophenylhydrazine correspond to those of samples produced by published procedures.[3]

Acetone 2,4,6-trinitrophenylhydrazone (**I**). - To 1.0 g. (41 mmol.) of 2,4,6-trinitrophenylhydrazine dissolved in 50 ml of solvent, [either ether (Baker, anhydrous 9244)or glyme] in a 250 ml. round bottom, single neck flask fitted with a dropper funnel, was added dropwise, with stirring, 5 ml. of reagent grade acetone (Baker 9006) dissolved in 25 ml. of solvent. Neither color change nor heat evolution were observed. After the reaction was stirred at room temperature for 12 hours, the solvent was removed *in vacuo* at room temperature. The solid residue was recrystallized using a *nitrogen purged* glyme/ligroine (40-60°) solvent pair. A second recrystallization in nitrogen-purged, boiling, 95% ethanol yielded a golden crystalline solid, 90% net yield, mp. 130-133°, lit.[9b] mp. 125°. The infrared spectrum of **I** in a KBr pellet, exhibits the same absorptions as those for samples produced by published methods;[1,2] there was no absorption (e.g. N-H) in the 3000-2840 cm^{-1} region. Proton magnetic resonance spectra:[7,8] (DMSO-d_6): δ1.97, s, 3H, $C\underline{H}_3$; δ2.04, s, 3H, $C\underline{H}_3$; δ3.29, s, 1H, $N\underline{H}$; δ8.83, 2H, s, aromatic.

Acetaldehyde 2,4,6-Trinitrophenylhydrazone (**II**). - To a solution of 41 mmole of trinitrophenylhydrazine is 50 ml. of glyme (or ether) in a 250 ml., round bottom, 3-neck flask (fitted with a pressure equalizing dropper funnel, a gas diffusion tube and a thermometer) cooled by an ice bath, was added dropwise 5 ml. of freshly depolymerized acetaldehyde[9] (bp. 24°). Neither heat evolution nor color change were observed. After stirring for 72 hours in a static nitrogen atmosphere, the solvent was removed in vacuo at room temperature leaving a red-brown powder, 90% yield, mp. 109-114°. This sample was used for spectral and chemical investigations without further recrystallization. Samples recrystallized from nitrogen purged ether melted between 124-127°. The infrared spectrum corresponds to the spectrum of samples produced by published procedures (no absorption, e.g. N-H, in the 3000-2840 cm^{-1} region). Proton magnetic resonance spectra:[7,8] (polysol-d):[7] δ1.93, d, 3H, $C\underline{H}_3$; δ3.32, bs, 1H, N$\underline{H}$; δ7.85, q, 1H, = C$\underline{H}$; δ8.75, 2H, aromatic.

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