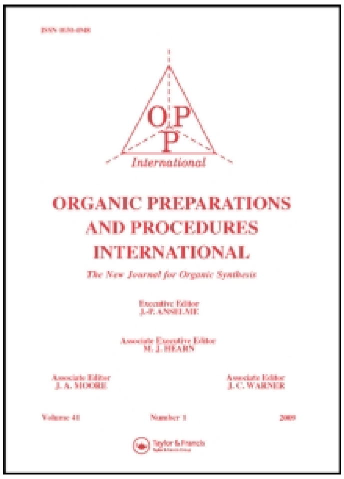

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PREPARATION OF N,N-DIMETHYLHYDRAZIDES

Stanley Wawzonek[a]
[a] Department of Chemistry, The University of Iowa, Iowa City, Iowa

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PREPARATION OF N,N-DIMETHYLHYDRAZIDES

Stanley Wawzonek

Department of Chemistry
The University of Iowa
Iowa City, Iowa 52242

Dimethylhydrazides of acetic[1] (67%), benzoic[2] (77%), isophthalic[3] (66%), and sebacic[3] (86%) acids are obtained in the yields shown by refluxing the corresponding phenyl esters with excess 1,1-dimethylhydrazine. Direct hydrazinolysis of alkyl esters with dimethylhydrazine occurs only with formates; esters of other aliphatic or aromatic acids are reported not to react[4]. The reaction was successful with esters of aromatic acids when catalyzed by sodium hydride or sodium methoxide and gave hydrazides in yields that varied from 14 to 80%[5].

$$RCOOC_6H_5 + (CH_3)_2NNH_2 \longrightarrow RCONHN(CH_3)_2 + C_6H_5OH$$

The present method avoids the use of acid chlorides and anhydrides for the preparation of these compounds[2] since phenyl esters can be prepared by the direct esterification of phenols using sulfuric and boric acids as catalyst[6].

Methyl benzoate behaved differently and gave a 34% yield of 1,1,1-trimethylhydrazinium benzoate after 65 hrs of reflux.

$$C_6H_5COOCH_3 + (CH_3)_2NNH_2 \longrightarrow (CH_3)_3\overset{+}{N}NH_2\ \overset{-}{O}COC_6H_5$$

displacement occurred in preference to hydrazinolysis. The structure of this compound was proved by conversion to trimethylhydrazinium iodide with hydriodic acid.

EXPERIMENTAL

1-Benzoyl-2,2-dimethylhydrazine. - Phenyl benzoate (19.8g, 0.1 mole) was refluxed with anhydrous 1,1-dimethylhydrazine (50 ml) for 45 hrs; tlc examination of the solution on silica indicated the absence of phenyl benzoate. The use of benzene as a solvent and excess 1,1-dimethylhydrazine gave an incomplete reaction in the same period of time. Removal of excess 1,1-dimethylhydrazine[7] by distillation followed by steam distillation left an aqueous solution of the hydrazide which was evaporated to dryness under reduced pressure. The resulting solid (15.7g) after recrystallization from a mixture of hexane and benzene melted at 100-105°; yield, 12.7g. The IR spectrum was identical to that of an authentic sample[2].

The analogous reaction with phenyl acetate and diphenyl sebacate required only 24 hrs for the disappearance of the ester. Diphenyl isophthalate[8] behaved differently and gave a solid gel of the hydrazide after two hours. Addition of benzene gave a suspension which was heated for an additional 22 hrs. This complication may account for the slightly lower yield of this dihydrazide. The hydrazide from sebacic acid melted at 137-138° (lit.[3], 136.5-137.5°) and that from isophthalic acid at 255-257° (lit.[3], 255-256°). 1-Acetyl-2,2-dimethylhydrazine had a boiling point of 104-106° (25 mm) (lit.[1], 80-81° (5 mm)) and gave an nmr spectrum similar to that reported[1].

1,1,1-Trimethylhydrazinium Benzoate. - Methyl benzoate (13.6g, 0.1 mole) was refluxed with 1,1-dimethylhydrazine (50 ml) for 65 hrs. Examination of the product by tlc on silica indicated the presence of methyl benzoate. Removal of the dimethylhydrazine and methyl benzoate by distillation under reduced pressure (2 mm) gave an oil which solidified when treated with acetone; yield, 6.75g. The solid was dissolved in water and the resulting solution after filtration and concentration under reduced pressure gave an oil which crystallized upon the addition of acetone; mp. 84.5-86.5° (uncor.). IR(nujol) 3.1(NH); 6.27μ(CO).

Anal. Calcd for $C_{10}H_{16}N_2O_2H_2O$: C, 56.07; H, 8.41; N, 13.08. Found: C, 56.38; H, 8.36; N, 12.86.

Reaction of Trimethylhydrazinium Benzoate with Hydriodic Acid. - The benzoate (1.96g) in water (50 ml) was treated with 47% hydriodic acid (1.9 ml) in water (10 ml). The aqueous solution after extraction with benzene and concentration under reduced pressure gave 0.3g (19%) of trimethylhydrazinium iodide, mp. 227° (dec.). The ir spectrum was identical with that of an authentic sample[9].

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