The Synthesis and Structure of 1,1,1-Trimethylhydrazinium 3-Methoxycarbonylpyrazole-5-carboxylate, a Typical Novel Intermediate for Acid-ester Synthesis

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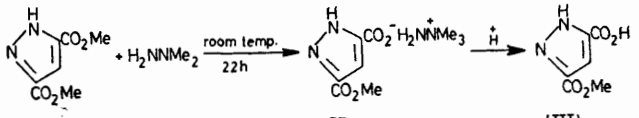
Summary 1,1-Dimethylhydrazine was observed to monodemethylate a dimethyl ester at room temperature to give a 1,1,1-trimethylhydrazinium-ester (II), whose subsequent treatment with acid gave an acid-ester (III); a single crystal *X*-ray analysis of (II) was carried out.

SYNTHESIS of compounds containing both an acid and an ester group (acid-esters) is tedious, particularly when the functional groups necessary for the formation of an anhydride, a common precursor for acid-esters, are not vicinal. We now report a new, simple acid-ester synthesis in which a dimethyl ester (I) is monodemethylated with excess 1,1-dimethylhydrazine, and the resulting 1,1,1-trimethylhydrazinium ester (II) converted to the corresponding acid-ester (III) (Scheme). The reaction was applicable to aliphatic, alicyclic, aromatic, and heterocyclic systems.

Half acid-esters of glutaric 1,2-cyclohexane, benzene, and 3,5-pyrazole were synthesized. The yield of the intermediate salts varies from 25—60% depending on the nature of the starting diester. The yield of acid-esters formed by adding acid to the salt was almost quantitative.



(I) (II) (III)

A preliminary characterisation of (II) was carried out by elemental, i.r. and n.m.r. spectral analyses. [δ (CF_3CO_2H) reference 2,2,3,3-tetradeuterio-3-(trimethylsilyl) propionate, 3·45 (NMe_3), 4·05 (OMe), 7·6 (arom. H); ν_{max} (KBr) 1730 (ester C=O), 1580 cm^{-1} (carboxylate C=O)]. Unequivocal structural proof of (II) was given by *X*-ray crystallography.‡

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‡ Details of the *X*-ray analysis will be published in *Acta Cryst.*