Ferric Chloride-catalysed Conversion of α-t-Butoxy- or α-Acetoxy-acrylonitriles into Imides

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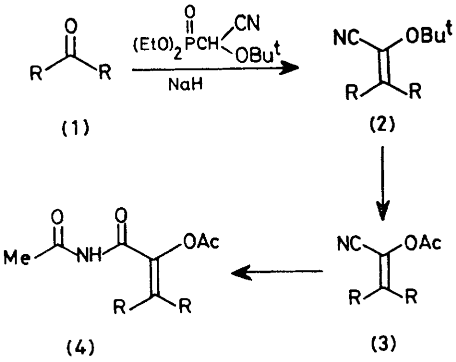
Summary Ferric chloride in acetic anhydride promotes the conversion of α-t-butoxy- or α-acetoxy-acrylonitriles into α-acetoxy-αβ-unsaturated imides by the formal addition of acetic acid across the C≡N bond; the structure of one of the products has been determined by *X*-ray crystallography.

We have recently devised an efficient synthesis of α-t-butoxyacrylonitriles (**2**) from carbonyl compounds (**1**).[1] In connection with our interest in developing the synthetic potential of (**2**), we sought to remove the $\mathrm{Bu^t}$ group in order to liberate the latent acyl cyanide. In the course of studying the acid-catalysed cleavage of ethers of this type, we observed a dramatic variation in the product distribution as a function of the Lewis acid catalyst.

The reaction of (**2**) with anhydrous zinc chloride (1·2 equiv.) in refluxing acetic anhydride [2 ml/mmol of (**2**)] for 15 min afforded the α-acetoxyacrylonitrile (**3**) in 90% yield. In contrast, the reaction of (**2**) with anhydrous ferric chloride (3·2 equiv.) in acetic anhydride[2] for 24 h at 25 °C furnished an entirely different product which was derived from (**3**) and differed from (**3**) in possessing the additional elements of acetic acid according to mass spectral and analytical data. Its n.m.r. spectrum, however, obfuscated the appropriate structural assignment in displaying three acetyl methyl signals at δ 2·21, 2·48, and 2·87 which could not be accurately integrated as a result of overlap with other signals. We therefore resorted to a single crystal *X*-ray diffraction study which established that the new product has the structure (**4**) (Scheme).†



SCHEME. $R = CH_2CH_2Ph$.

Crystal data: $C_{23}H_{25}NO_4$, space group $P2_1/c$, $a = 10{\cdot}627(3)$, $b = 15{\cdot}951(6)$, $c = 12{\cdot}615(5)$ Å, $\beta = 98{\cdot}41(3)°$, $U = 2115(1)$ Å^3, $D_m = 1{\cdot}18$ and $D_c = 1{\cdot}191$ g ml^{-1}, $Z = 4$. Diffraction data ($2\theta_{max} = 50°$, Mo-K_α graphite monochromatized radiation) were collected with a Syntex P1 autodiffractometer using the θ–2θ scan technique. Of the 3217 measured reflections, 1513 were considered observed and used for the refinement. The structure was solved using direct methods[3] and refined by full-matrix least-squares techniques to $R = 10{\cdot}0\%$.‡ Hydrogen atoms were included at fixed positions and all other atoms were refined anisotropically. Atomic types were assigned on the basis of molecular geometry and refined isotropic thermal parameters leading to the structure (**4**). The puzzling n.m.r. spectrum of (**4**) was attributed to the existence of a tautomer of (**4**) in solution.

Literature procedures for the synthesis of imides from nitriles require drastic conditions to effect the addition of a carboxylic acid across a C≡N bond.[4] The easy transformation of (**2**) to (**4**) prompted a survey of the scope of the ferric chloride–acid anhydride procedure for the synthesis of imides. We found, however, that this new procedure was limited to the preparation of imides from α-t-butoxy- or α-acetoxy-acrylonitriles.§

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table may be obtained as a supplementary publication (No. 22086, 6 pp.) from the British Library. For details of obtaining this material, see Notice to Authors No. 7, Index Issues of *J.C.S. Perkin I* or *II*, 1976.

‡ The carbon atoms C(4), C(5), C(6), and C(11) were disordered and no model could be determined which adequately accounted for this result.

§ For example, cinnamonitrile and 3-phenylpropionitrile were recovered unchanged from a $FeCl_3$–Ac_2O mixture which converted α-acetoxycinnamonitrile into its imide in 76% yield.

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[3] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368. All calculations were performed on a CDC6400 computer using programs from the Northwestern University Crystallographic Library of Dr. J. A. Ibers and a data reduction program written in this laboratory.
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