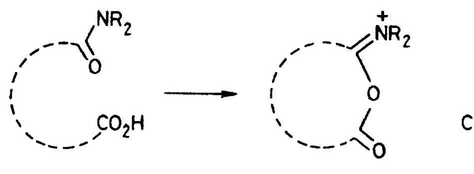
Acylation of Tertiary Amides. Formation of 1-Acyloxyiminium Salts and 1-Acyloxyenamines

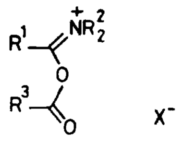
By William E. Bottomley and Gerhard V. Boyd*
(*Department of Chemistry, Chelsea College, London* SW3 6LX)

Summary Tertiary carboxamides are acylated at the oxygen atom by benzoyl or acetyl chloride in the presence of silver trifluoromethanesulphonate; if the resulting 1-acyloxyiminium salts contain hydrogen atoms at positions 2 or 4 they can be deprotonated to yield unstable 1-acyloxy-enamines or -dienamines, which have been trapped by reaction with 4-phenyl-1,2,4-triazoline-3,5-dione.

Whereas intramolecular acylation of *N*-substituted monoamides (**1**) of dicarboxylic acids proceeds readily in the presence of acetic anhydride and perchloric acid to yield stable cyclic isoimidium perchlorates (**2**),[1] the formation of well defined acyclic analogues (**3**) has not been reported.[2] Most of the published work concerns the action of acyl halides on dimethylformamide, which results in reversible *O*-acylation to give the iminium halides (**3a**);[3] the adduct with acetyl bromide, for example, is completely dissociated into its components at room temperature.[4] Little is known about acylations of amides derived from higher acids: the salt (**3b**) has been proposed[5] as an intermediate in the complex reaction of trichloroacetyl chloride with *NN*-diethylphenylacetamide and n.m.r. studies suggest[4] that the equilibrium mixture of acetyl bromide and *NN*-dimethylacetamide contains at most 15% of the adduct (**3c**) at −53 °C.



(1) (2)

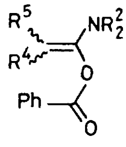


(3)

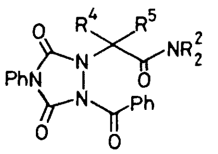
a; R^1 = H, R^2 = Me, R^3 = Me or Ph, X = Cl or Br
b; R^1 = PhCH$_2$, R^2 = Et, R^3 = CCl$_3$, X = Cl
c; R^1 = R^2 = R^3 = Me, X = Br
d; R^1 = H, R^2 = Me, R^3 = Ph, X = CF$_3$SO$_3$
e; R^1 = R^3 = Ph, R^2 = Me, X = CF$_3$SO$_3$
f; R^1 = R^2 = R^3 = Me, X = CF$_3$SO$_3$
g; R^1 = R^2 = Me, R^3 = Ph, X = CF$_3$SO$_3$
h; R^1 = PhCH$_2$, R^2 = Et, R^3 = Ph, X = CF$_3$SO$_3$
i; R^1 = Ph$_2$CH, R^2 = Et, R^3 = Ph, X = CF$_3$SO$_3$

We now report that tertiary amides of formic, benzoic, acetic, phenylacetic, and diphenylacetic acid react smoothly with acetyl or benzoyl chloride in dichloromethane solution at room temperature in the presence of silver trifluoromethanesulphonate (silver 'triflate') to give the acyloxyiminium triflates (**3d**—**i**) in essentially quantitative yields.

The salts are stable in solution if moisture is rigorously excluded. They show ester carbonyl and imine absorptions at 1827—1778 and 1715—1645 cm^{-1}, respectively. The ^{1}H n.m.r. spectra of compounds (**3d**) and (**3g**) indicate that the *N*-methyl groups are non-equivalent and that the signals of all protons are shifted downfield from their positions in the spectra of the parent amides: dimethylformamide shows δ(CH) 8·10 and δ(NMe) 3·27 and 3·16, while the salt (**3d**) shows δ(CH) 8·55 and δ(NMe) 3·35 and 3·18; *NN*-dimethylacetamide shows δ(CMe) 2·08 and δ(NMe) 3·02 and 2·93; the corresponding signals of the salt (**3g**) are at δ 2·82, 3·64, and 3·58, respectively. The action of aniline on compound (**3g**) afforded solely benzanilide and dimethylacetamide. This is in contrast with the reaction of the dimethylformamide–benzoyl chloride adduct with aniline, which yields mainly *NN*-dimethyl-*N'*-phenylformamidine.[3b,c]



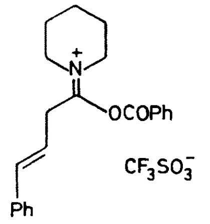
(4)



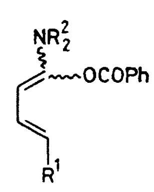
(5)

a; R^2= Me, R^4 = R^5 = H
b; R^2 = Et, R^4 = H, R^5 = Ph
c; R^2 = Et, R^4 = R^5 = Ph

The iminium triflates (**3g**—**i**), which contain hydrogen atoms at C-2, are readily deprotonated by triethylamine or pyridine to yield the unstable 1-acyloxyenamines (**4a**—**c**, respectively), which could only be obtained in solution.[6]

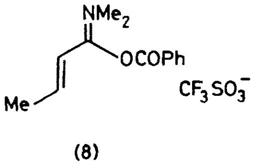


(6)

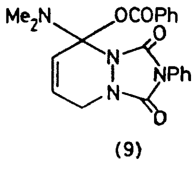


(7)

a; R^1 = Ph, NR$^2_2$ = piperidino
b; R^1 = H, R^2 = Me



(8)



(9)

The i.r. spectra of these compounds exhibit ester carbonyl bands at 1740—1730 cm^{-1} and typical enamine absorptions at 1640 cm^{-1}. The first two acyloxyenamines yielded the crystalline adducts (**5a**, **b**),† the products of an 'acyl-ene reaction',[7] when the deprotonation of the iminium salts (**3g**, **h**) was carried out in the presence of 4-phenyl-1,2,4-triazoline-3,5-dione.

Benzoylation of the piperidide of styrylacetic acid gave the iminium triflate (**6**); the derived benzoyloxydienamine (**7a**) (ν_{max} 1743 and 1640 cm^{-1}) persisted in solution for at least 1 h at room temperature. Deprotonation of the salt (**8**), obtained from *NN*-dimethylcrotonamide, gave the unstable base (**7b**), which yielded the Diels–Alder adduct (**9**)† on treatment with *N*-phenyltriazolinedione.

We thank the S.R.C. for a studentship (to W.E.B.) and May & Baker Ltd. for their support.

(*Received, 2nd June* 1980; *Com.* 582.)

---

† Satisfactory analytical and spectroscopic data were obtained for all isolated compounds.

[1] G. V. Boyd and R. L. Monteil, *J. Chem. Soc., Perkin Trans.* 1, 1978, 1338.

[2] For a useful summary of acid amide–carboxylic acid halide adducts, see W. Kantlehner, in 'Advances in Organic Chemistry,' eds. H. Böhme and H. G. Viehe, Vol. 9, Part II, Wiley, New York, 1979, p. 42.

[3] (a) H. K. Hall, *J. Am. Chem. Soc.*, 1956, **78**, 2717; (b) H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, 1959, **92**, 837; (c) D. E. Horning and J. M. Muchowski, *Can. J. Chem.*, 1967, **45**, 1247.

[4] G. J. Martin and N. Naulet, *Tetrahedron Lett.*, 1976, 357.

[5] A. J. Speziale, L. R. Smith, and J. E. Fedder, *J. Org. Chem.*, 1965, **30**, 4303.

[6] A number of 1-acyloxyenamines have been obtained by the action of silver or triethylammonium carboxylates on 1-chloroenamines (L. Ghosez and J. Marchand-Brynaert, in 'Advances in Organic Chemistry,' eds. H. Böhme and H. G. Viehe, Vol. 9, Part I, Wiley, New York, 1976, p. 475).

[7] G. V. Boyd, R. L. Monteil, P. F. Lindley, and M. M. Mahmoud, *J. Chem. Soc., Perkin Trans.*, 1, 1978, 1351.