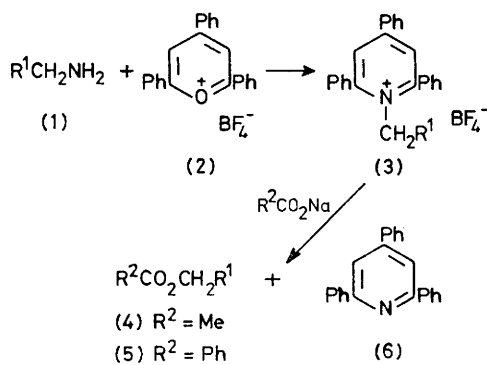


Pyridines as Leaving Groups in Synthetic Transformations: Conversion of Amines into Esters¹

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Summary Primary amines RCH_2NH_2 are converted into acetates ($MeCO_2CH_2R$) and benzoates ($PhCO_2CH_2R$) in a two-step process: (a) reaction with triphenylpyrylium tetrafluoroborate and (b) pyrolysis of the pyridinium tetrafluoroborate so obtained with the sodium carboxylate.

THE limitations of known synthetic procedures available for the replacement of amino by oxygen functionality² motivated us to develop a two-step process *via* *N*-substituted pyridinium salts for the conversion of amines into esters in good yields.



Primary amines (1) with 2,4,6-triphenylpyrylium tetrafluoroborate (2)³ in ethanol yield the corresponding *N*-substituted 2,4,6-triphenylpyridinium salts (3) (Table). The salt is mixed with 2 equiv. of sodium acetate or sodium benzoate, and 2,4,6-triphenylpyridine to serve as a flux. This mixture is heated *in vacuo* to *ca.* 200 °C; 2,4,6-tri-

phenylpyridine (6) is eliminated as in the analogous preparation of isocyanates,⁴ and the corresponding ester distills out of the reaction mixture in 60–85% yield (Table).

TABLE. *N*-Substituted pyridinium tetrafluoroborates and their conversion into acetates and benzoates

Tetrafluoroborate salts (3) ^a	Acetates (4) ^b		Benzoates (5) ^b	
	<i>N</i> -Substituent	Yield %	Yield %	Yield %
Me	87	217–218 ^c	65	70
Et	73	164–165 ^d	79	60
Bu ⁿ	67	201–202	75	85
PhCH ₂ CH ₂	77	271	70	—
2-Picolyl	55	218–219	60 ^e	68 ^f
3-Picolyl	76	166–168	78 ^g	75 ^h
Benzyl	69	196–197	70	85
2-Methylbenzyl	94	178	70	—

^a Satisfactory analytical and spectral data were obtained for all these new compounds. ^b Identical by spectral comparison with authentic material unless otherwise indicated. ^c Lit., m.p. 215–216 °C, R. Lombard and A. Kress, *Bull. Soc. chim. France*, 1960, 1528. ^d Lit., m.p. 164–165 °C, see ref. in c. ^e Identified as the hydrochloride, m.p. 92–93 °C (lit., m.p. 94–95 °C, K.-B. Augustinsson and H. Hasselquist, *Acta Chem. Scand.*, 1964, **18**, 1006). ^f Picrate salt, m.p. 159–160 °C (lit., m.p. 161–162 °C, J. H. Boyer and L. T. Wolford, *J. Amer. Chem. Soc.*, 1958, **80**, 2741). ^g Identified as the hydrochloride, m.p. 95 °C (lit., m.p. 96–98 °C, see ref. in c). ^h Methiodide salt, m.p. 158–159 °C (lit., m.p. 159 °C, L. Panizzon, *Helv. Chim. Acta*, 1941, **24**, 24 E).

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¹ Cf. the series Heterocycles in Organic Synthesis. Part VIII, M. J. Cook, A. R. Katritzky, and G. H. Millet, submitted to *Heterocycles*.

² See e.g. 'Weygand/Hilgetag, Preparative Organic Chemistry,' 4th edn., eds. G. Hilgetag and A. Martini, Wiley, New York, 1972, p. 342.

³ R. Lombard and J.-P. Stephan, *Bull. Soc. chim. France*, 1958, 1458.

⁴ J. B. Bapat, R. J. Blade, A. J. Boulton, J. Epszajn, A. R. Katritzky, J. Lewis, P. Molina-Buendia, P.-L. Nie, and C. A. Ramsden, *Tetrahedron Letters*, 1976, 2691.