

2-(2-Imidazolyl)acetophenones *via* Aroylation of *N*-Substituted 2-Methylimidazoles

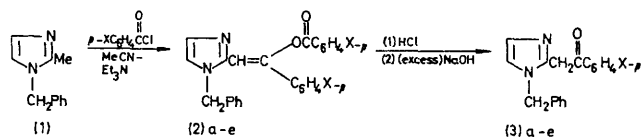
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Summary *N*-Substituted 2-methylimidazoles, on treatment with aroyl chlorides in MeCN-Et₃N, are transformed into (2a-f) in a simple, high yield process; hydrolysis thereof produces the title compounds (3a-f).

RECENT studies¹ have shown *N*-substituted imidazoles to react with benzoyl chloride in MeCN-Et₃N furnishing 2-benzoylated derivatives. Our interest in the electrophilic substitution pattern of 1,2-disubstituted imidazoles² prompted examination of the behaviour of the latter with various benzoyl chlorides under comparable conditions.

Compound (1) in MeCN-Et₃N was treated dropwise with 1 mol. equiv. of benzoyl chloride at 5–25° for 2–4 h; addition of water and ether afforded in ca. 90% yield (based on halide) compound (2a): ν_{\max} 1730 (C=O), 1660



(C=C), and 1240 cm⁻¹ (C–O–C); δ (CDCl₃) 8.40–8.15 (m, 2H, ArH), 7.70–6.80 (m, 15H, ArH), 6.67 (s, 1H, CH=C) and 5.17 (s, 2H, CH₂Ph). Use of 0.5 mol. equiv. of the imidazole or conducting the reaction in dimethylformamide did not influence the yield; the use of dimethyl sulphoxide, though, did lower it to 30%.

The method appears to be general. Substituted benzoyl chlorides with (1) in Et₃N-containing MeCN gave (2b–e) in excellent yields; apparently variations in the C=O electrophilicity affect neither the course nor the yield of the reaction. Compound (2f) under these conditions, was

¹ E. Regel and K. H. Buechel, *Ger. Offen.* 1,926,206/1970 (*Chem. Abs.*, 1971, **74**, 31,754f); *Ger. Offen.* 1,956,711/1971 (*Chem. Abs.*, 1971, **75**, 49,086v); C. G. Begg, M. R. Grimmett, and Lee Yu-Man, *Austral. J. Chem.*, 1973, **26**, 415.

² E. F. Godefroi, H. J. J. Loozen, and J. Th. J. Luderer-Platje, *Rec. Trav. chim.*, 1972, **91**, 1333.

³ B. Tertov, V. V. Burykin, and I. D. Sadekov, *Khim. geterotsikh. Soedinenii*, 1969, 520 (*Chem. Abs.*, 1969, **71**, 12,4328y).

TABLE

Comp.	X ^a	M.p. °C	Yield (%) ^b	Comp.	X ^a	M.p. °C
(2a)	H	146	97	(3a)	H	204 ^c
(2b)	Me	156	80	(3b)	Me	89
(2c)	NO ₂	ca. 163 ^c	95	(3c)	NO ₂	110
(2d)	Cl	152	93	(3d)	Cl	92
(2e)	OMe	170	80	(3e)	OMe	109
(2f) ^d	H	140	93	(3f) ^d	H	101

^a *para*-Substituents. ^b Based on crude product, with m.p. slightly below that of the analytical material. ^c HCl salt. ^d 2-(1-methylimidazolyl) derivative.

formed from 1,2-dimethylimidazole. All enol esters were characterized by combustion analyses and n.m.r. and i.r. data ($\nu_{C=O}$ 1730–1740 cm⁻¹). Compounds (2a–f) were hydrolysed with refluxing 3*N*-HCl (1–3 h) to furnish the phenacylimidazoles (3a–f).

Formation of (2a–f) is surprising as, to our knowledge, nonactivated 2-methyl substituents in *N*-substituted imidazoles are reluctant to partake in electrophilic processes. 1,2-Dimethylimidazole, for example, undergoes both lithiation³ and hydroxymethylation² at C-5. Compounds (2a–f) are most probably formed *via* an irreversible *O*-arylation of anionic intermediates formed from (3a–f) thus displacing all prior equilibria in favour of the final conjugated system. Our observation that (3a), on treatment with benzoyl chloride in MeCN-Et₃N, is converted into (2a) substantiates this view.

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