Metal-catalysed Addition of β-Dicarbonyl Compounds to the Nitrile Carbon of Benzoyl Cyanide. Synthesis of 1-Amino-1-benzoyl-2,2-diacylethenes

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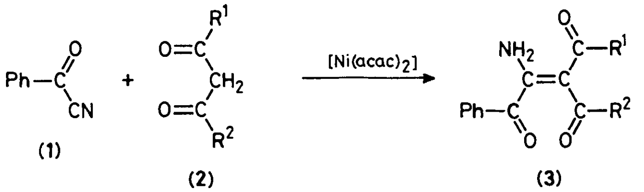
The complex $[Ni(acac)_2]$ (Hacac = pentane-2,4-dione) selectively catalyses addition of the intercarbonylic carbon atom of β-diketones to the cyano group of benzoyl cyanide, whereas usual basic organic catalysts lead to attack on the carbonyl carbon atom with displacement of the C≡N group.

Acyl cyanides are useful reagents as electrophiles in organic synthesis especially for mild acylation reactions.[1] As a rule nucleophiles (*e.g.* water, alcohols, amines, C–H activated compounds, *etc.*) preferentially attack the CO group leading to (O)C–C(≡N) bond fission.[1] In particular, reaction of the β-dicarbonyl compound ethyl benzoylacetate with benzoyl cyanide gives, in the presence of a two-fold excess of dimethylaniline, ethyl dibenzoylacetate and hydrogen cyanide.[2]

We have found that addition of C–H acidic β-diketones can be directed to the C≡N triple bond in the presence of catalytic amounts of $[Ni(acac)_2]$(Hacac = pentane-2,4-dione) to give 1-amino-1-benzoyl-2,2-diacylethenes (Scheme 1) smoothly in high yields.†



Scheme 1: a; $R^1 = R^2 = Me$
b; $R^1 = Me, R^2 = Ph$
c; $R^1 = R^2 = Ph$

The crystal structure of compound (**3b**) (Figure 1) has been determined by *X*-ray diffraction.‡ The molecule, apart from the two phenyl rings, is approximately planar, this planar arrangement being stabilized by a hydrogen bond between O(3) and H(N) (2.60 Å). The bond distances are fairly high for the C(2)–C(3) double bond (1.394 Å) and low for the single C–C bonds in the β-diketone skeleton (1.449—1.465 Å), thus suggesting extended resonance throughout the molecule.

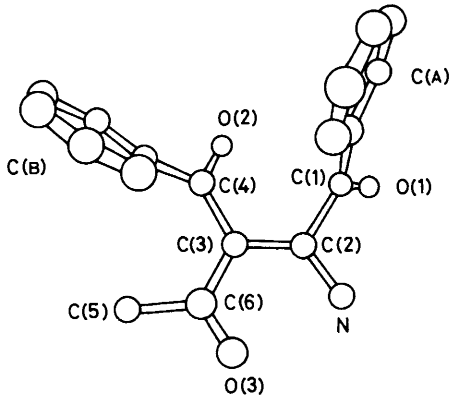


Figure 1. The molecular structure of 1-amino-1,2-dibenzoyl-2-acetylethene (**3b**). Principal bond lengths (Å): C(A1)–C(1) 1.475(7); C(1)–C(2) 1.524(7); C(2)–C(3) 1.394(6); C(3)–C(4) 1.449(6); C(B1)–C(4) 1.499(6); C(3)–C(6) 1.465(7); C(6)–C(5) 1.509(7); C(6)–O(3) 1.236(6); C(4)–O(2) 1.235(6); C(1)–O(1) 1.217(6); C(2)–N 1.325(6).

The success of this synthesis implies that the order of electrophilic character normally found in the CO and CN groups of benzoyl cyanide is reversed in the presence of the $[Ni(acac)_2]$ catalyst. Most likely the key stage involves co-ordination of benzoyl cyanide to the metal through the nitrile nitrogen. This leads to the expected[5] increase of the electrophilicity of the CN carbon atom, so favouring attack on it by the metal-co-ordinated β-diketonate nucleophile. Complexes bearing the anion of (**3**) as a ligand were, in fact, isolated and characterized in independent experiments from the reaction of nickel β-diketonate complexes with benzoyl cyanide. Thus, the reaction mechanism implies preliminary ligand substitution of $[Ni(acac)_2]$ by the β-diketone (**2**), followed by electrophile co-ordination, C–C bond formation, and substitution of the functionalized ligand in ensuing steps. A similar mechanistic proposal was made for the metal-catalysed synthesis of pyrimidines from C_2N_2 and β-dicarbonyls.[6]

This study shows that catalysis *via* metal–acac complexes not only is a useful alternative to the base-catalysed addition of nucleophiles to electrophiles as observed in the reaction of β-dicarbonyl compounds with C_2N_2,[6] but it also may be the only synthetic approach when basic conditions orient the nucleophilic attack towards CN substitution.

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† $[Ni(acac)_2]$ (4×10^{-1} mol dm^{-3}); (**1**) = (**2**) = 2 mol dm^{-3}; solvent, refluxing 1,2-dichloroethane; reaction time 2.5 h. Reactions were conducted under argon. All products precipitated on cooling: (**3a**) and (**3c**) at 20 °C; (**3b**) at −20 °C; yields: (**3a**), 73; (**3b**), 87; (**3c**), 73%; m.p.s: (**3a**), 164; (**3b**), 146; (**3c**), 197 °C.The compounds are pale yellow crystalline solids, which have good elemental analyses and were characterized by i.r., u.v.–visible, ^1H n.m.r., and mass spectroscopy, and, for (**3b**), by *X*-ray analysis.

‡ *Crystal data for* (**3b**): $C_{18}H_{15}NO_3$, $M = 293.32$, monoclinic, space group $P2_1/n$, $a = 15.575(7)$, $b = 10.322(5)$, $c = 9.168(5)$ Å, $\gamma = 92.4(1)^\circ$, $U = 1473$ Å^3, $Z = 4$, $F(000) = 616$. The intensity data were collected on a fully automated Philips PW 1100 four-circle diffractometer, using Mo-K_α radiation ($\lambda = 0.7107$ Å). 1659 Reflections, having $I \geqslant 2.5\sigma(I)$, were measured to $\theta = 25^\circ$. The structure was solved by direct methods by using Multan.[3] The final *R*-factor was 6.2%. All the calculations were performed using SHELX.[4] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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