

The Reaction of Benzylcyanide with Chalcones

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The reaction of benzylcyanide with chalcones (I) was reinvestigated. Depending upon the reaction conditions and chalcones (I a–c) either α -phenylcinnamitrile (IIIa) or the open chain Michael adduct (IV) was obtained. The structures of all the compounds have been established by elemental analysis and spectral data.

INTRODUCTION

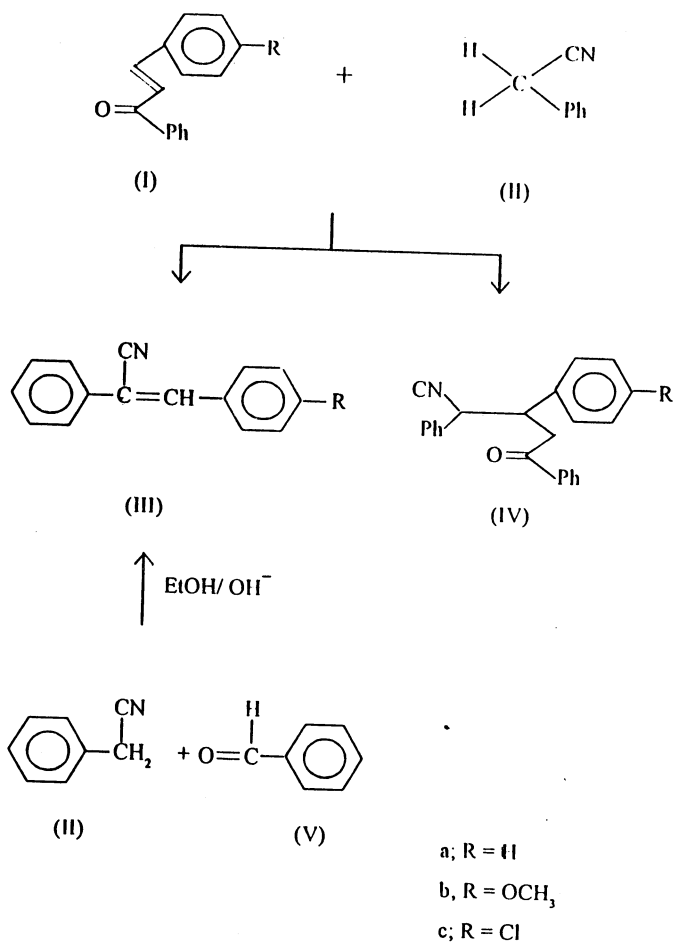
The reaction of chalcones (1,3-diphenyl-2-propen-1-ones) (I) with active methylene compounds containing a cyano group is still ambiguous and variable^{1–11}. The reaction of chalcone with benzylcyanide⁹ in equimolar quantities in presence of sodium ethoxide or triethylamine gave the corresponding mono-adduct 3-aryl-4-benzoyl-2-phenyl-butyronitrile. However, bis-condensation product has also been reported in presence of sodium methylate¹². As a part of on going research programme in our laboratories^{13–16} and in view of the above we carried out the reaction of benzylcyanide with chalcones (I) under different experimental conditions.

RESULTS AND DISCUSSION

The reaction of chalcone (Ia) with benzylcyanide (II) in presence of DMF and anhydrous K_2CO_3 (method A) gave α -phenylcinnamitrile (IIIa). IR spectrum of (IIIa) exhibited a strong peak at 2220 cm^{-1} for the $—CN$ group. The mass spectrum of the compound showed the characteristic fragmentation pattern¹⁷ of both stilbene and conjugated nitriles and occur via rearrangement, cyclisation and loss of fragments $—CH_3$, $—CH_2CN$ and HCN .

The structure was also confirmed by an independent synthesis from benzylcyanide (II) and benzaldehyde (V) in presence of base. However, the same reaction when carried out in presence of DMSO and anhydrous K_2CO_3 (method B), ethanol and piperidine (method C), C_6H_6 -TEBA-anhydrous K_2CO_3 (method D) there resulted an open chain Michael adduct 2,3-diaryl-4-benzoylbutyronitrile (IV). Compound (Ib) under method B and (Ic) under reaction conditions of methods A, B and C remained unchanged (Scheme I), whereas method D resulted in Michael addition product (IV).

Therefore, from the experimental results it seems that method D is most suitable for the synthesis of (IV) from substituted chalcones (I), whereas in only one case (method A) (IIIa) resulted from chalcone (Ia).



SCHEME-I

EXPERIMENTAL

All the m.p.s. were determined in open capillary tubes and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer spectrophotometer 150 P (ν_{\max} in cm^{-1}). PMR spectra were recorded in CDCl_3 on a Perkin-Elmer Model EM-360 (60 MHz) using TMS as internal standard (chemical shifts in δ ppm) and mass spectra were recorded on a Jeol D300 spectrometer. Homogeneity of all the compounds was checked by TLC using silica gel-G as adsorbent and visualization was done in iodine chamber.

1,3-Diarylpropanones (I a-c)

These compounds were obtained by the condensation of equimolar amounts of appropriate acetophenones and benzaldehydes. Compound Ia (85%) m.p.

56–57°C (lit.¹⁸ 56–57°C); Ib (86%), m.p. 75°C (lit.¹⁹ 75°C); and Ic (82%), m.p. (lit.¹⁹ 103°C) have been obtained as pale yellow crystalline solids.

α -Phenylcinnamonitrile(IIIa)

Method A: Mixture of Ia (2.0 g, 0.01 mol), benzylcyanide (1.1 g, 0.01 mol), anhydrous K_2CO_3 (4.0 g) and DMF (30 mL) was refluxed for 12 h. The reaction mixture was cooled and filtered. The residue in the flask was extracted with boiling DMF (2 \times 20 mL) and filtered. The combined filtrate was concentrated under reduced pressure and the residue diluted with water (50 mL). The reaction mixture on cooling in refrigerator afforded a solid which was filtered, dried and crystallised in petroleum ether as cream coloured crystals; yield 0.8 g (26%), m.p. 85° (lit.²⁰ 85–86°C). (Found: C, 87.34; H, 5.77; N, 6.79. $C_{15}H_{11}N$ requires C, 87.76; H, 5.40; N, 6.82%). IR: 2220 cm^{-1} $\nu(CN)$; PMR ($CDCl_3$): 7.3–8.0 (11H, m-C—H and Ar—H). MS: m/z 205 [M^+] 204, 190, 178, 165, 102, 89, 76 and 51.

The structure of IIIa was finally confirmed by m.m.p. Co-TLC superimposable IR spectra with an authentic sample prepared by an independent synthesis from benzylcyanide (II) with benzaldehyde (V) in presence of sodium hydroxide and ethanol.

2-Phenyl-3-substituted phenyl-4-benzoylbutyronitrile (IV)

Method A: A mixture of Ib (2.3 g, 0.01 mol), benzylcyanide (1.1 g, 0.01 mol), anhydrous K_2CO_3 (4.0 g) and DMF (30 mL) was refluxed for 12 h and the reaction mixture worked up as above. The residue on recrystallisation from ethanol afforded IVb; yield 1.2 g (35%), m.p. 128°C. (Found: C, 81.57; H, 6.44; N, 3.78%. $C_{24}H_{21}NO_2$ requires: C, 81.08; H, 5.95; N, 3.94%). IR: 2220 cm^{-1} $\nu(CN)$ and 1680 ($C=O$). Compound (Ic) under similar condition was recovered unchanged.

Method B: A mixture of Ia (2.0 g, 0.01 mol), benzylcyanide (1.1 g, 0.01 mol), anhydrous K_2CO_3 (4.0 g) and DMSO (30 mL) was refluxed for 12 h and the reaction mixture worked up as in method A. The resulting compound IVa was crystallised as white crystals from ethanol; yield 1.0 g (32%), m.p. 110°C. (Found: C, 84.67; H, 6.03; N, 5.02. $C_{23}H_{19}NO$ requires: C, 84.88; H, 5.89; N, 4.30%). IR: 2220 cm^{-1} $\nu(CN)$ and 1680 cm^{-1} $\nu(C=O)$. PMR ($CDCl_3$): 3.30–3.90 (3H, m,—CH—CH₂), 4.45 (1H, d, C—H) and 7.00–8.00 (15H, m, Ar—H).

Compounds Ib and Ic under similar conditions remained unchanged.

Method C: A mixture of Ia or Ib (0.01 mol), benzylcyanide (0.01 mol), ethanol (60 mL) and piperidine (8 mL) was refluxed for 12 h. It was cooled and treated with dil. HCl and kept in refrigerator. An oily compound separated was dissolved in ethanol to afford analytical samples of IV. Compounds IVa, yield 0.9 g (29%) and IVb, yield 1.4 g (41%) obtained by this method were confirmed on the basis of m.m.p., Co-TLC and superimposable IR spectra of an authentic sample prepared by methods A and B.

Compound Ic under similar conditions remained unchanged.

Method D: A mixture of chalcone I (0.01 mol), benzylcyanide (0.01 mol), benzene (60 mL), TEBA (0.2 g) and anhydrous K_2CO_3 (4.0 g) was refluxed for 10 h. The reaction mixture was filtered and the residue washed with benzene

(2 × 30 mL). The combined filtrate was concentrated and petroleum ether (40–60°C) was added till turbidity appeared. The solution was warmed and then left at room temperature. The crystalline compound separated afforded analytical samples of (IV).

Compounds IVa, yield 1.0 g (32%) and IVb, yield 1.7 g (50%) were obtained and characterised by comparing with an authentic sample obtained by above methods. Compound IVc, yield 1.6 (46%), m.p. 139°C. (Found: C, 76.87; H, 5.48; N, 3.65% C₂₅H₁₈ NOCl requires: C, 76.75; H, 5.04; N, 3.89%). IR 2220 cm⁻¹ ν(CN) and 1680 cm⁻¹ ν(C=O).

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