

Studies on Conjugated Nitrones: Addition of Hydrogen Cyanide on to Conjugated Nitrones

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Summary The elements of hydrogen cyanide and of methanol add in a 1,3-manner to conjugated nitrones.

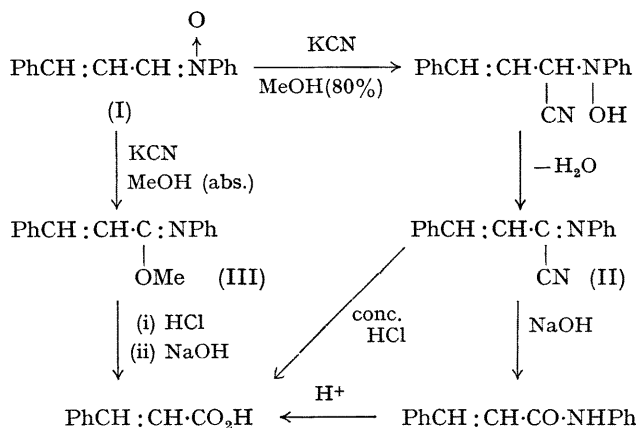
DIPOLAR cycloadditions of unsaturated compounds to nitrones are well known.^{1,2} Conjugated nitrones have recently been prepared,³ and their dipolar cycloadditions studied. We now describe nucleophilic addition of HCN on to conjugated nitrones, and some reactions of the novel cyano-anils thus obtained.

Potassium cyanide was added, in excess, to a solution of the nitron (I) in 80% methanol, and after 2–3 hr. at room temperature the solvent was distilled off under reduced pressure. The residue, after dilution with water, was extracted with ether. Evaporation of the ether layer gave a yellow pasty mass which was crystallised from petrol to give (II), m.p. 73–75° (80%). β -Furylvinyl-*N*-phenylnitron similarly yielded the corresponding cyano-anil in 75% yield (m.p. 100°).

The cyano-anil structure of (II) is supported by u.v., i.r., and n.m.r. spectral evidence. [I.r.: ν_{\max} 970 (CH=CH *trans*), 1610 (C=N), and 2250 cm^{-1} (C≡N)]. The strong absorption at 2250 cm^{-1} suggests that the cyano-group is attached to the unsaturated carbon as in α -amino-nitriles. Quenching of this frequency has been observed.⁴ Two protons are observed in the τ 3–4 region of the n.m.r. spectrum (60 MHz, CDCl_3), and the u.v. spectrum showed the presence of a styrene chromophore.

Acid hydrolysis of (II) gave cinnamic acid in almost

quantitative yield. Hydrolysis of (II) with dilute caustic alkali gave an unsaturated anilide, cinnamanilide.



When (I) was treated with KCN in absolute methanol, an unsaturated imine ether (III) was obtained, which after hydrolysis with hydrochloric acid then with alkali was converted into cinnamic acid.

The ready cleavage of the C=N bond is in contrast to an earlier report⁵ in which cinnamylideneaniline is said not to be affected by aqueous acid even under reflux. The stability of the C=N bond seems to be due to extended conjugation.

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⁴ N. Singh, J. S. Sandhu, and S. Mohan, unpublished results.

⁵ G. Peine, *Ber.*, 1884, **17**, 2117.