α-Hydroxy-β-*p*-tolylcinnamonitrile, a Stable Enol[1]

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In a study of the boron trifluoride etherate-catalysed rearrangements of certain α-cyano-epoxides, we have found that the catalysed reaction of 2,3-epoxy-*trans*-2-phenyl-3-*p*-tolylpropionitrile (I)† in benzene gives a mixture of α-cyanophenyl-*p*-tolylacetaldehyde (II; 47%), the product of *p*-tolyl migration, and a second product believed to be that derived from phenyl migration, phenyl-*p*-tolylpyruvonitrile (III; 53%). The percentage composition of the mixture was assigned from the integrated n.m.r. spectrum using the singlet absorptions at τ 0·53 and 4·88 for the aldehydic proton of (II) and H_a of (III), respectively. The assignment of structure (III) to the second product is based on the n.m.r. and i.r. (nitrile absorptions at 4·50 and 4·55 μm. and a single carbonyl absorption at 5·85 μm.) spectra of the mixture and the fact that it is converted into (V) (see below). The n.m.r. spectral absorption at τ 4·88 atributed to (III) was not lost when the sample dissolved in carbon tetrachloride was allowed to stand with intermittent shaking over a 3 hr. period in the presence of deuterium oxide.

Separation of (II) and (III) was made difficult by the fact that (II) was readily decarbonylated when treated with base,

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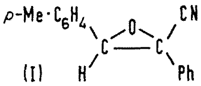
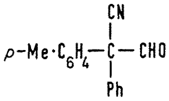
† All new compounds have given satisfactory elemental analyses.

or during chromatography on alumina, to phenyl-*p*-tolylacetonitrile (IV). When an ether solution of (II) and (III) was extracted with aqueous base, not only was partial decarbonylation of (II) to (IV) observed but the n.m.r. spectral absorption at τ 4·88 was lost.

Acidification of the basic extract produced a solid, m.p. 114—115°, which exhibited n.m.r. spectral absorptions (CCl_4, internal Me_4Si) centred at τ 2·70 and 2·85 (multiplets, 9H, aromatic), 4·05 [broad singlet, 1H, OH (exchangeable with D_2O)], and 7·67 and 7·69 (singlets, 3H, *p*-methyls of the *cis*- and *trans*-enols). The i.r. spectrum was characterized by hydroxy (3·09 μm.) and cyano (4·50 μm.) absorptions and the u.v. spectrum (ethanol) exhibited rather broad absorptions at 290 (log ϵ 4·28) and 235 nm. (log ϵ 4·08).‡ The mass spectrum§ of this compound was also accommodated from considerations of the reasonable cracking patterns expected from both the keto- and enol forms of the molecule.

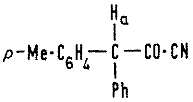


(I)



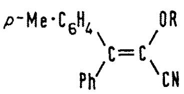
$p\text{-Me}\cdot C_6H_4-C(CN)(Ph)-CHO$

(II)



$p\text{-Me}\cdot C_6H_4-C(H_a)(Ph)-CO\cdot CN$

(III)



(V) R = H

(VI) R = Me

From this spectral information the structure α-hydroxy-β-(*p*-tolyl)cinnamonitrile (V) is assigned to this compound.¶ The n.m.r. spectral absorptions at τ 7·67 and 7·69 are interpreted as due to the *p*-tolyl methyl groups of the *cis*- and *trans*-isomers of (V) and that the interconversion of these two isomers is slower than the n.m.r. time scale at 38°.

The acidic character of (V) was further shown by its ready reaction with ethereal diazomethane to produce the corresponding enol methyl ether (VI). The u.v. spectrum of (VI) showed essentially no overall changes compared with that of (V) in either shape, wavelengths of absorption, or molar absorptivities.‡ This, together with the n.m.r. spectrum of (V), establishes (V) as a stable enol with little if any equilibrium to the keto-form (III).

The form (III) appears to be reasonably stable in aprotic solvents, *e.g.* benzene and carbon tetrachloride. Neither contact with water in the work-up of the reaction mixture nor in the attempted deuterium–proton exchange in the n.m.r. tube appears to generate (V), as evidenced by n.m.r. spectroscopy; identical spectra were obtained whether the original reaction mixture was directly evaporated or washed with water until almost neutral and evaporated. We, as yet, have no information on the stability of (III) in protic solvents.

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‡ The shorter-wavelength u.v. absorption in both (V) and (VI) showed evidence of some fine structure.

§ Mass-spectral analysis was performed by Dr. R. G. Cooks using the AEI MS9 mass spectrometer and a direct insertion probe.

¶ We have synthesized the fourth isomer of this group of compounds, α-cyano-α-*p*-tolylacetophenone, the product of cyanide migration, and shown it to be different from (V).

[1] For previous paper in this series, see R. N. McDonald and R. N. Steppel, *J. Amer. Chem. Soc.*, 1969, **91**, 782.