A Cyanide Ion-catalysed Reaction of 3-Phenylprop-2-ynal with Methanol. Evidence for an Oxy-cumulene Intermediate

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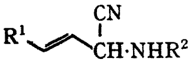
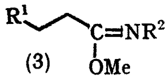
WE showed[1] that treatment of cinnamaldehyde cyanohydrin with cyanide ion in methanol gives methyl hydrocinnamate. This reaction appears to proceed *via* the keten (1a) by a mechanism similar to that of the base-catalysed conversion[2] of cyano-amines (2) into imino-esters (3) *via* the ketenimine (1b). If the intermediacy of (1) in these reactions is correct, then a 3-substituted propadienone[3] intermediate (8) formed under similar conditions from a suitable precursor should produce equal amounts of the stereoisomeric methyl esters (9) and (10); this would be required from the stereochemistry of addition of methanol to (8). We report results which support these expectations.

(1) a; $X=O$
b; $X=NR^2$

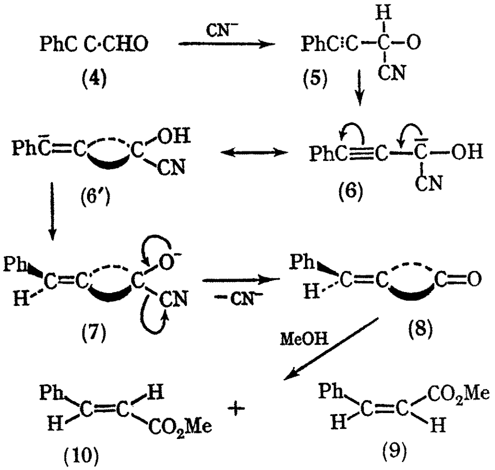


(2)



Treatment of 3-phenylprop-2-ynal (4) with an equivalent of potassium cyanide in methanol afforded a geometrical mixture of methyl cinnamates (9) and (10) (90%; distilled 80%). That this is a mixture of equal amounts of *cis*- and *trans*-isomers was shown by its n.m.r. spectrum ($CDCl_3$) (two signals of equal intensity for OMe at τ 6·20 and 6·32). The *cis*- and *trans*-isomers were separated by g.l.c. on 25% DC-560 silicone oil on Chromosorb P at 220° and were identical in all respects with authentic samples.

The reaction presumably proceeds by the mechanism shown in the Scheme where the phenylpropadienone intermediate (8) is formed from the carbanion (6) *via* the anion (7). Addition of methanol to (8) then affords the stereoisometric esters (9) and (10).



SCHEME

We believe the reaction[4] of 3-phenylprop-2-ynal with acetone cyanohydrin in the presence of triethylamine which yields 2-cyanoprop-2-yl *cis* and *trans*-cinnamate in *ca.* 8% yield also proceeds *via* the intermediate (8). In this case the stereoisomeric esters arise from the addition of acetone cyanohydrin to (8).

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[3] The decomposition of some mixed anhydrides has recently been suggested as proceeding through dimerization of a transient disubstituted propadienone intermediate. G. A. Taylor, *Chem. Comm.*, 1968, 1314. See also G. H. Birnum and C. N. Matthews, *J. Amer. Chem. Soc.*, 1968, **90**, 3842.

[4] L. A. Yanovskaya, Kh. Shakhidayatov, and V. F. Kucherov, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1967, 2553 (*Chem. Abs.*, 1968, **69**, 67061P).