A Tertiary Phosphine-catalyzed Reaction of Acrylic Compounds with Aldehydes

Ken-ichi MORITA, Zennosuke SUZUKI and Hiromitsu HIROSE

The Basic Research Laboratories, Toyo Rayon Company, Ltd., Kamakura

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We report here a novel reaction which gives new vinyl monomers. Reaction of acrylonitrile or methyl acrylate with various aldehydes in the presence of tricyclohexylphosphine as a catalyst furnished vinyl compounds 1 to 12 in 70 to 90% yields.^{1,2}) A typical example is as follows: reaction of 34.4 g (0.4 mol) of methyl acrylate, 26.4 g (0.6 mol) of acetaldehyde and 0.7 g (2.5 mmol) of tricyclohexylphosphine in 12 ml of dioxane in an atmosphere of nitrogen at 120-130°C for 2 hr afforded compound 9 in a yield of 85% based on converted methyl acrylate (conversion 23%).

 $CH_2=CHX + RCHO \stackrel{{}_{}_{}_{}}{\underset{}_{}^{}_{}}^{P}CH_2=C \stackrel{{}_{}_{}_{}}{\overset{{}_{}_{}}{\underset{}}^{N}CH(OH)R}$ 1, X = CN; $R = CH_3$. 2, CN; CH_2CH_3 . 3, CN; (CH₂)₂CH₃. 4, CN; CH(CH₃)₂. 5, CN; (CH₂)₆.

CH₃. 6, CN; C₆H₅. 7, CN; p-Cl-C₆H₄. 8, CN; p-CH₃-C₆H₄. 9, CO₂CH₃; CH₃. 10, CO₂CH₃, CH₂CH₃. 11, CO₂CH₃; (CH₂)₂CH₃. 12, CO₂CH₃; C₆H₅.

Structures for compounds 1 to 12 were assigned on the basis of their elemental analyses, the NMR spectra, the infrared spectra (nitrile band at 2229 cm^{-1} and double bond band at 1623 cm^{-1} for compounds 1 to 8; ester band between 1917 and 1722 cm⁻¹ and double bond band between 1631 and 1635 cm^{-1} for compounds 9 to 12), and the ultraviolet absorption spectra (maximum between 202.5 and 206.5 m μ in methanol).

The structures of compound 1 and 9 were further confirmed by conversion of them into 1,4-dicyano-4-vinyl-1-cyclohexene,⁴⁾ and 1,4-dicarbomethoxy-

2) It has been reported³) that the reaction of acry-lonitrile and triphenylphosphine with benzaldehyde in the presence of alcohol at 140-175 °C afforded *trans*-4-phenyl-3-butenenitrile and triphenylphosphine oxide. 3) R. Oda, T. Kawabata and S. Tanimoto,

Tetrahedron Letters, **1964**, 1653. 4) C. S. Marvel and N. O. Brace, *J. Am. Chem. Soc.*, **71**, 37 (1949).

4-vinyl-1-cyclohexene,⁴⁾ respectively, by treatment with boiling acetic anhydride and pyridine. 2-Cyano-1,3-butadiene and 2-carbomethoxy-1,3butadiene dimerize readily under these conditions.

The possible mechanisms⁵) of the reaction are depicted below.

mechanism I



It is conceivable that if triphenylphosphine is 5) used for the reaction the zwitterion I (R=phenyl) can isomerize to an ylid (III) by a proton transfer which then undergoes irreversible reaction with aldehydes to produce triphenylphosphine oxide and an olefin as Oda^{3} reported. The absence of the interconversion I \rightleftharpoons III when R is alkyl is supported by the absence of 1,4-dicyanobutene in the product when acrylonitrile is dimerized in the presence of catalytic quantities of trialkylphosphines such as tri-*n*-butylphosphine or tricyclohexylphosphine.⁶)

$$\begin{array}{c} R_{3}\overset{1}{P}CH_{2}-\overset{1}{C}HCN \rightleftarrows R_{3}\overset{1}{P}\overset{1}{C}HCH_{2}CN \\ I & III \\ & \downarrow CH_{2}=CHCN & \downarrow CH_{2}=CHCN \end{array}$$

CH₂=C-CN

NCCH=CHCH₂CH₂CN CH2CH2CN

6) Cf. M. M. Baizer and J. D. Anderson J. Org. Chem., **30**, 1357 (1965); P. Charardes, C. Grard, P. Lafont and M. Thiers (to Rhnoe-Poulene), French Pat. 1226081 (1964).

¹⁾ The novel reaction can be called Carbinol. Addition.