The Reaction of Enamines with Acetonecyanohydrin

By Yujiro NOMURA, Takiko SHIMURA and Yoshito TAKEUCHI

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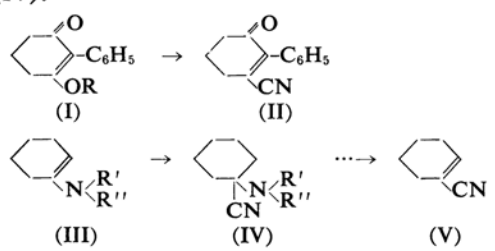
Betts and Davey[1] reported that the alkoxy group in the enol ethers (I) of 2-phenylcyclohexane-1, 3-dione was replaced by a cyano group by a reaction with acetonecyanohydrin, yielding 2-phenyl-3-cyano-2-cyclohexen-1-one (II). In connection with the resemblance of the properties of enol ethers and enamines, the reaction of the enamines (III) of cycloalkanone with acetonecyanohydrin has been investigated and found to yield aminonitrile (IV).



(I) (II)

(III) (IV) (V)

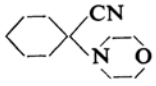
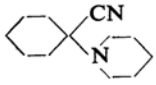
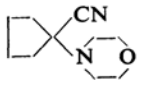
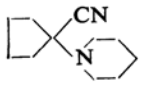
No further reaction to cyanocycloalkene (V) could be observed, even when IV was treated with thionyl chloride in pyridine.[2] Thus, the reaction of 1-morpholino-1-cyclohexene, 1-piperidino-1-cyclohexene, 1-morpholino-1-cyclopentene and 1-piperidino-1-cyclopentene with acetonecyanohydrin in chloroform in the presence of triethylamine gave 1-cyano-1-morpholinocyclohexane (VI) (m.p. 44～45°C), 1-cyano-1-piperidinocyclohexane (VII) (m. p. 67～68°C), 1-cyano-1-morpholinocyclopentane (VIII) (m. p. 53～54°C), and 1-cyano-1-piperidinocyclopentane (IX) (b. p. 88°C/3 mmHg) respectively. Of these aminonitriles, VIII and IX are new substances.

The identity of these products was confirmed by a comparison with authentic samples prepared by the condensation of cycloalkanone-cyanohydrin with morpholine or piperidine. The infrared spectra of these aminonitriles (VI—IX) in a carbon tetrachloride solution had an absorption at 2225～2230 cm^{-1}, indicating the presence of a cyano group.

1) B. E. Betts and W. Davey, *J. Chem. Soc.*, **1961**, 3333.

2) H. O. House, V. Paragamian, R. S. Ro and D. J. Wluka, *J. Am. Chem. Soc.*, **82**, 1461 (1960).

TABLE I. AMINONITRILES PRODUCED BY THE REACTION OF ENAMINE WITH ACETONECYANOHYDRIN

Aminonitrile	No.	Yield %	B. p. °C/mmHg	M. p. °C	IR cm^{-1}	N % Calcd.	N % Found
	VI	74 (almost quanti.)	127~133/4[a]	44~45[a] (45)	2230 1122 (2230) (1120)	14.42	14.31
	VII	57 (47)	(120~121/3)	67~68[b] (67~68)	2230	14.57	14.80
	VIII	55 (almost quanti.)	98~99/2.5	53~54 (52~53)	2225 1117	15.54	15.61
	IX	48 (50)	88/3 (104/4)	n_D^{19} 1.4908 ($n_D^{20.8}$ 1.4901)	2225	15.71	15.70

a) The reported[3] boiling point of VI is 120°C/1 mmHg, and the melting point is 35°C. It was prepared by the catalytic reduction (Pd-charcoal) of 1-cyano-1-morpholino-2-iodocyclohexanein methanol in the presence of triethylamine.

b) The reported[4] melting point of VII is 59°C. It was prepared from piperidine hydrochloride, sodium cyanide and cyclohexanone in an aqueous ethanol solution.

Experimental

All temperatures are uncorrected. The infrared spectra were determined with a Nihon Bunko Model Koken DS 301 spectrophotometer.

The Reaction of Enamines with Acetonecyanohydrin.—To a solution of enamine (0.1 mol.) and triethylamine (0.1 mol.) in 100 ml. of chloroform, one molar equivalent of acetonecyanohydrin was added. After the exothermic reaction had subsided, the mixture was heated under reflux for two hours. The solution was then cooled and poured into 300 ml. of water which had been neutralized with 6 N hydrochloric acid (Congo red). The layers were separated, and the aqueous layer was extracted with three 50 ml. portions of ether. The combined chloroform layer and ether extracts were washed with dilute hydrochloric acid and then with water. After the solution had been dried over anhydrous magnesium sulfate and the solvent had been removed, the crude aminonitrile appeared; this was purified by distillation at reduced pressure or by recrystallization from ethanol.

The aminonitriles obtained by this procedure are listed in Table I along with the results obtained by the condensation of cycloalkanonecyanohydrin with morpholine or piperidine (in parentheses).

Department of Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo

3) E. Fusco, G. Bianchetti and S. Rossi., *Gazz. Chim. Ital.*, **91**, 825 (1961).

4) A. Kötz and P. Merkel *J. prakt. Chem.*, [2], **111**, 74 (1926); G. Le Ny and Z. Welvart, *Compt. rend.*, **245**, 434 (1957); Parke, Davis & Co., Brit. Pat. 851782 (1960) [cf. *Chem. Abstr.*, 55, 10477 (1961)].