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PHOTOCYCLOADDITION OF ACETYLCYANIDE TO OLEFINS

Y. Shigemitsu, Y. Odaira, and S. Tsutsumi
Department of Chemical Technology, Faculty of Engineering,
Osaka University, Osaka, Japan

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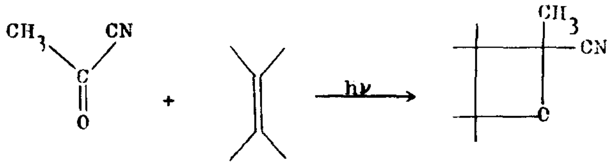
Since the formation of oxetanes by means of the photocycloaddition of a carbonyl compound to olefins was discovered by Paterno and Chieffi[1], and subsequently studied by Büchi and his co-workers[2], many simple oxetanes have been photochemically prepared[3]. As part of serial studies of photochmical formation of oxetanes having an important functional group, we wish to report here the synthesis of a new oxetane (III) having a cyano group directly bonding to a carbon atom of a trimethyleneoxide ring by the photocycloaddition of acetylcyanide (I) to an olefin such as 1,1-diphenylethylene, α-methylstyrene, norbornene or 2-methyl-2-butene.



I II III

A solution of acetylcyanide (0.05-0.2 mole) and an olefin (0.1-0.3 mole) was irradiated with a 1 KW high-pressure mercury arc under the nitrogen stream at room temperature for 6-20 hours. After the irradiation, acetylcyanide was almost disappeared. The oxetanes were characterized by infrared and nuclear magnetic resonance spectra, molecular weight measurement, and elemental analysis. The oxetanes obtained are listed in Table I. From Table I it is obvious that the photocycloaddition of acetylcyanide to the olefins affords oxetanes in good yields except in the case of α-methylstyrene.

From the results of our previous study,[*,4] it is confirmed that these reactions proceed through the $n \rightarrow \pi^*$ excitation of the carbonyl group. Acetylcyanide has a spectrum consisting a broad $n \rightarrow \pi^*$ transition band at $\lambda_{max}=309$ mμ ($\varepsilon=23$) and this band occurs a bathochromic shift relative to other acetyl derivatives.[**] This red shift may be due to the resonance effect of the cyano group on the carbonyl part, making it more easy to promote the n electron of the carbonyl group.

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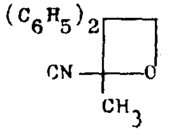
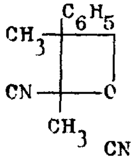
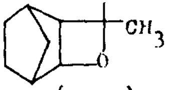
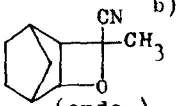
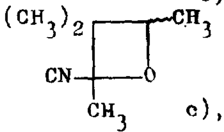
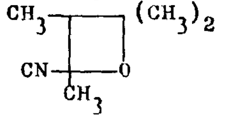
[*] A broad band at $\lambda_{max}=309$ mμ occurs a hypsochromic shift when the solvent is changed from a nonpolar to a polar one. In addition, acetylcyanide is photoreduced in a hydrogen donating solvent to give lactonitrile.

[**] For example, acetaldehyde, acetone, and acetylchloride show the $n \rightarrow \pi^*$ transition band at $\lambda_{max}=293.4$, 279, 235 mμ, respectively.

TABLE I

Photocycloaddition of Acetylcyanide to Olefins

Olefin	Oxetane	Yield %[a]	NMR τ	IR cm^{-1}
1,1-Diphenylethylene		52	2.96(m) 4.95(d) 5.10(d) 8.61(s)	2270 968
α-Methylstyrene		18	2.80(m) 5.06(d) 5.68(d) 8.07(s) 8.62(s)	2270 980
Norbornene	b)  (exo-)	40	5.13(d) 7.32(d) 8.45(s) 7.55-9.10(m)	2270 985
	b)  (endo-)	37	5.06(t) 7.12(t) 8.30(s) 7.30-9.00(m)	2260 992
2-Methyl-2-butene	c),d) 	28	5.49(q) 5.72(q) 8.43-8.90 (complex absorption)	2260 1050
	c),e) 	10	7.39(q) 8.35(s) 8.61(s) 8.66(s) 8.78(d)	2260 960

a) Basis on consumed olefin.

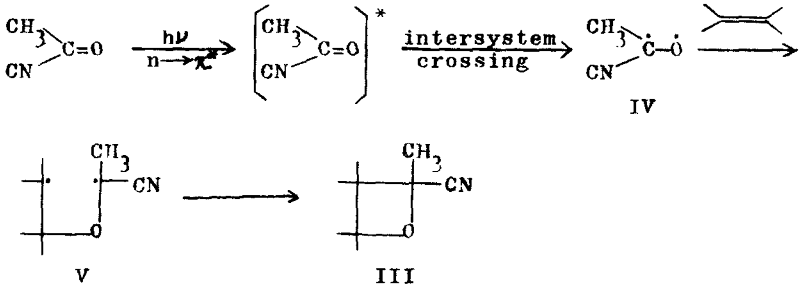
b) These two isomers were seperated by chromatography over silica gel and were characterized by NMR spectra based on the information reported by Kumler and his co-workers with respect to the α- and α'-chlorocamphors.[5]

c) These two isomers were isolated by the preparative gas chromatography and the structure was determined by NMR spectra. It is generally found that the NMR spectra of the oxetanes show the hydrogens α to oxygen at 5.0-6.0τ while hydrogen β to oxygen on the ring occurs at 6.4-7.4τ.[3c)]

d) The NMR spectrum suggests that two possible isomers are present.

e) The NMR analysis of this oxetane shows that only one isomer is present. Consequently, 2-methyl-2-butene affords totally three isomers of oxetanes.

The formation of oxetanes would involve the following sequence



The reaction would proceed through the attack of $n\rightarrow\pi^*$ triplet state (IV) to an olefin to produce a biradical intermediate (V). In this case, the biradical (V) may be very stabilized by the resonance effect of the cyano group. This stabilization of the biradical (V) must be responsible for the successful synthesis of the oxetanes from acetylcyanide relative to other acetyl derivatives. A further evidence which supports this conclusion is a photochemical formation of oxetanes from a cyanoester in good yields[6]. In this case, an oxetane is not obtained when a simple ester is used as a carbonyl component.

Further studies of the photochemical formation of oxetanes having an important functional group will be presented elsewhere.

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