

A PHOTOCHEMICAL ADDITION OF
ACETIC ACID TO STRAINED CYCLOALKYNES AND NORMAL ALKYNES

K. Fujita, K. Yamamoto and T. Shono

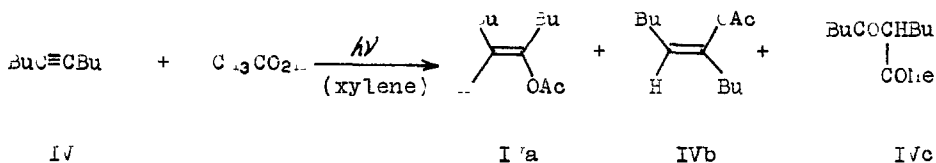
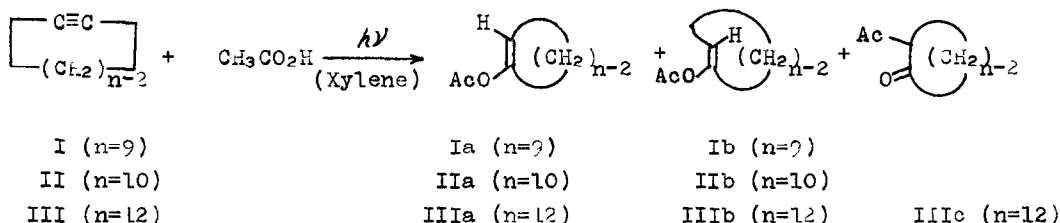
Department of Synthetic Chemistry, Kyoto University,
Kyoto, Japan

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The photochemical polar addition of a protic solvent (carboxylic acid, alcohol, etc) to a medium size cycloalkene (from cyclohexene to cyclooctene) has been well established¹, whereas larger size cycloalkenes were reported to show cis-trans isomerization under the same reaction condition^{1a,b}. On the other hand, the photochemical polar addition of a solvent to related cycloalkynes has not received any attention as yet².

We wish to report a novel photochemical reaction of a cycloalkyne (cyclononyne, cyclodecyne or cyclododecyne) or decyne-5 with acetic acid to yield cis and trans enol acetates³ under the reaction condition where the corresponding alkene is absolutely inert. The cycloalkynes and decyne-5 did not give the enol acetates without the irradiation of UV light. This would be the first observation of the photochemical polar addition of a protic solvent to a cycloalkyne.

A solution of cyclononyne (1.0 g) and xylene (3 ml) in acetic acid (250 ml) was irradiated for 60 hours with a low pressure mercury lamp under an atmosphere of nitrogen. After the solution was concentrated in vacuo at room temperature, the products, Ia (0.07 g) and Ib (0.02 g), were isolated from the residue with column chromatography (Silicagel, Benzene). The major product, Ia, was assigned to 1-acetoxy-cis-cyclononene on the basis of spectral and chemical behaviors. The ir spectrum of Ia showed the characteristic absorption of an enol acetate moiety at 1750 and 1680 cm^{-1} , and the base catalyzed hydrolysis of Ia gave cyclononane. The following nmr and mass spectra of Ia gave further



support for the proposed structure. Nmr: 4.35 τ triplet (1H, CH=C, J=8.5Hz), 7.5-8.0 τ multiplet (4H, C=CC₂), 7.95 τ singlet (3H, OCOCH₃) and 8.0-8.8 τ multiplet (10H, CH₂) m/e=122 (M⁺-CH₃CO₂H) (the molecular peak was not observed). A conclusive evidence for the structural assignment was obtained from the comparison of Ia with the authentic specimen prepared from the acid catalyzed reaction of cyclononane with acetic anhydride. From the observation that this acid catalyzed reaction afforded only one enol acetate, Ia seems to have cis-cyclononene geometry which is expected to be thermodynamically more stable than the trans isomer.

The spectral data indicated that Ib was an isomeric enol acetate. Ir spectrum: 1710 and 1690 cm⁻¹, mass spectrum: 122 (M⁺-CH₃CO₂H), Nmr spectrum; 4.9 τ doublet (1H, CH=C, J=4.0Hz), 7.5-8.0 τ multiplet (4H, C=CC₂), 7.92 τ singlet (3H, OCOCH₃) and 8.0-8.8 τ multiplet (10H, CH₂). Compound Ib afforded cyclononane in a base catalyzed hydrolysis and isomerized slowly to Ia at room temperature, which was detected by nmr technique. These spectral and chemical behaviors suggested that Ib was 1-acetoxy-trans-cyclononene. The characterization of the geometries of Ia and Ib was also supported by the estimation of the nmr chemical shift of the olefinic proton on the basis of the shielding effect of acetoxy group, that is, the proton of Ib was expected to be more shielded than that of Ia⁵.

A similar irradiation of cyclododecyne (1.0 g) in acetic acid (250 ml) in the presence of xylene (3 ml) gave IIb (0.05 g) and a trace of IIa. Both IIa and IIb afforded cyclodecanone upon hydrolysis. Structural assignments of IIa and IIb were carried out by the similar procedure to those described above. IIa: Ir spectrum; 1750 and 1680 cm^{-1} , Nmr spectrum; 4.90 τ triplet (1H, CH=C, $J=8.5\text{Hz}$), 7.4-8.0 τ (4H, C=CCH₂), 7.96 τ singlet (3H, OOCCH₃) and 8.0-8.5 τ multiplet (12H, CH₂), mass spectrum; 136 ($\text{M}^+-\text{CH}_3\text{CO}_2\text{H}$). IIb; Ir spectrum; 1740 and 1680 cm^{-1} , Nmr spectrum; 4.95 τ doublet (1H, CH=C, $J=4.0\text{Hz}$), 7.4-8.0 τ multiplet (4H, C=CCH₂), 7.96 τ singlet (3H, OOCCH₃) and 8.0-8.8 τ multiplet (12H, CH₂), mass spectrum; $m/e=136$ ($\text{M}^+-\text{CH}_3\text{CO}_2\text{H}$).

A similar photochemical reaction (irradiation of 70 hr) of cyclododecyne or decyne-5 with acetic acid gave IIIa (1%), IIIb(2%) and IIIc(3%) or IVa (6%), IVb(7%) and IVc(9%), respectively³. Structural assignments of IIIa-c and IVc were carried out by the comparison of those compounds with the authentic specimens. The structures of IVa and IVb were determined on the basis of the spectral and chemical behaviors. Since the product IIIc or IVc was formed from the irradiation of IIIa,b or IVa,b respectively, IIIc or IVc seems to be a secondary product⁵.

Use of decyne-5 as a filter of the light markedly decreased the yield of the products in the photochemical reaction of decyne-5 regardless of the existence of xylene. Xylene did not show any effect on the yield of the reaction of decyne-5 or cyclododecyne, whereas it considerably enhanced the reaction of cyclononyne or cyclodecyne. Thus, it is interesting to note that the function of xylene as a sensitizer was observed not in the alkyne free from strain (cyclododecyne or decyne-5) but in the strained alkyne⁶ (cyclodecyne and cyclononyne). This phenomenon may be related to the strain relief of the latter alkyne in the excited state⁷.

References

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- (2) A photochemical addition of alcohol (a), carboxylic acid (b) or amine (c) to diphenylacetylene was reported. In the last reaction, it was suggested that the reactive species was the excited-singlet of diphenylacetylene.
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- (3) The reaction was stopped in the low conversion.
- (4) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry" 2nd Edition, Pergamon Press, New York, 1969, p 134-5.
- (5) Photochemical isomerizations of some enol acetates have been reported. (a) A. Yon'ev, M. Gorodetsky and Y. Mazur, *J. Am. Chem. Soc.*, 86, 5208 (1964), (b) D. Belluš and P. Hrdlovič, *Chem. Rev.*, 67, 599 (1967).
- (6) From the thermodynamic data for the isomerization of cyclic allenes to cyclic alkynes, it was said that cyclononyne and cyclodecyne had an appreciable strain of ring and more than 11-carbons cyclic alkynes were free from strain. W. A. Moor and H. R. Ward, *J. Am. Chem. Soc.*, 85, 86 (1963)
- (7) The geometry of the lowest excited acetylenic bond was suggested to be a trans-ethylene type. (a) C. K. Ingold and W. King, *J. Chem. Soc.*, 2702, 2704, 2708, 2725, 2747 (1953). (b) R. S. Mulliken, *Can. J. Chem.*, 36, 10 (1958). (c) R. Hoffmann, *Tetrahedron*, 22, 521 (1966). If the excited state have such a geometry, the distance between the terminus carbons (C₁ and C₄) in a plane ($C_1=C_4$) was roughly estimated to be 3.9Å, whereas the corresponding distance in the straight acetylene was nearly equal to 4.3Å.