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[2π + 2σ + 2π] CYCLOADDITION UNDER HIGH PRESSURE

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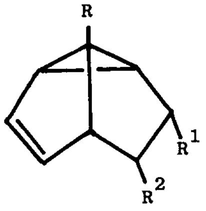
Abstract: The meta photocycloadduct (2) of anisole and cis cyclo-octene undergoes a homo Diels-Alder reaction with dialkyl butynedioates under high pressure but the corresponding photoadduct (6) from toluene gives the "ene" product (7) with these dienophiles under similar conditions.

The homo Diels-Alder reaction of ethenylcyclopropane systems, in principle, offers a convenient route to cycloheptane derivatives but few studies have been reported on this reaction and [2π + 2π] cycloadditions are greatly preferred in many potentially suitable cases.[1] In the course of our investigations into chemical transformations of meta photocycloadducts (1) of arenes and ethenes, we have found both [2π+2π] and [2π+2σ+2π] pathways to be available with 4-phenyl-1,2,4-triazoline-3,5-dione, tetracyanoethylene, and chlorosulphonyl isocyanate.[2] Less powerful dienophiles are generally unreactive with (1) under thermal conditions and, in particular, dialkyl butynedioates gave no identifiable products with the ethenylcyclopropane systems even in sealed tubes at 220°C. We now report that at ambient temperature under 11 kbar pressure the meta photocycloadduct (2) of anisole and cis cyclo-octene undergoes essentially quantitative addition to such ethynes.

A solution of dimethyl butynedioate (1.3 g) and (2) (2.0 g) in dichloromethane (total volume 5 ml) was subjected to 11 kbar for 15 hours after which the starting materials had completely reacted to give one product by t.l.c. together with minor amounts (<5%)of polymeric material. Analytical and mass spectrometric data of chromatographically purified product were consistent with a 1:1 adduct of (2) and the ester. The homo Diels-Alder adduct structure (3) was assigned on the basis of the spectroscopic data: ^{1}H δ values ($CDCl_3$ 220 MHz), 6.03 (1H, dd + fine splitting, J's = 9,5,1 and 1 Hz), 5.77 (1H, dd + fine splitting, J's = 9, 5.5, and 1 Hz), 3.84 (3H, s), 3.77 (3H, s), 3.42 (3H, s), 3.31 (1H, br dd, J's = 5.5 and 5.0 Hz), 3.20 (1H, dd + fine splitting, J's = 5.5 and 5.0), 2.80 (1H, m, J's = 9 and 4 Hz), 2.41 (1H, dd + fine splitting, J's = 5.5, 4.0, and 1 Hz), 2.14 (1H, br dd, J's = 9 and 5 Hz), and 1.9-1.1 p.p.m. (12 H, overlapping m's); ν_{max} = 1730 and 1633 cm^{-1}. Attempts to promote the conversion of (3) to its Cope isomer (4) failed but irradiation of (3) at 254 nm in ethyl acetate solution resulted in the ready formation of the intramolecular [2π+2π] cycloaddition isomer (5).

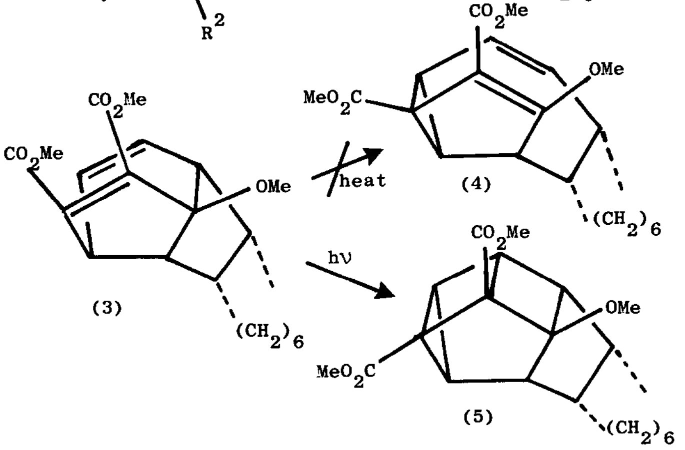
No high pressure reaction was observed for derivatives of (1) which had hydrogen at the 1-position but at 11 kbar the toluene-cis cyclo-octene adduct (6) and the

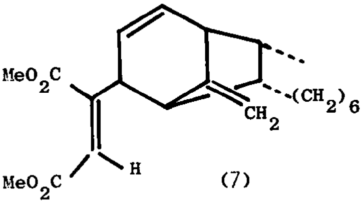


(1) R=H, Me, OMe, R^1,R^2=alkyl or alkoxy
or R^1=OAc, R^2=H

(2) R=OMe, R^1-R^2=-$(CH_2)_6$-

(6) R=Me, R^1-R^2=-$(CH_2)_6$-





(7)

acetylenic ester reacted to give the "ene" adduct (7) as the major product.[3] We are currently investigating mechanistic aspects of these reactions and, while the effectiveness of the 1-methoxy group in promoting the homo Diels-Alder process would seem to suggest some degree of polarity in the transition state, the absence of any relationship between the rate of the reaction and solvent polarity discounts the involvement of a dipolar species comparable with that involved in other cycloaddition reactions.[4]

There is an enormous volume of literature concerned with cycloadditions under pressure.[5] It is important to note that formation of (3) represents the first example of a homo Diels-Alder process of an ethenylcyclopropane system under pressure and illustrates the great potential of the technique as a synthetic procedure.

References and Notes

1. See for example S.Nishida, I.Moritani and T.Teraji, J.Org.Chem., 1973, 38, 1878.
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3. R.S.Sheridan, J.Amer.Chem.Soc., 1983, 105, 5140, reports similar products from the m-xylene-cyclopentene adduct and 4-phenyl-1,2,4-triazoline-3,5-dione at atmospheric pressure.
4. R.Gompper, Angew.Chemi.Internat.Edn., 1968, 8, 312.
5. N.S.Isaacs, "Liquid Phase High Pressure Chemistry", Wiley, Chichester (U.K.), 1981, pp. 216-227.

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