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DIRECT PHOTOLYSIS OF DIMETHYLDIAZOMALONATE IN THE PRESENCE OF SOME OLEFINS AND ACETYLENES

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SUMMARY

Reactions of carbenes and carbenoids have recently aroused increasing interest because of their wide application for the synthesis of new compounds.

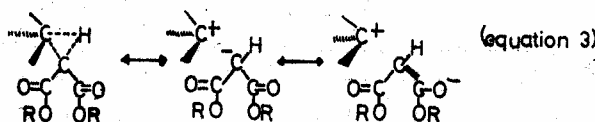
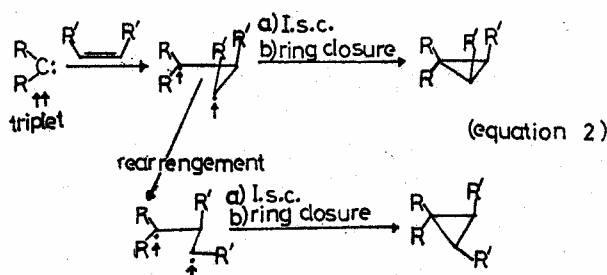
In this work, direct photolysis of dimethyl diazomalonate in the presence of define such as 2,4,4-trimethyl—2-pentene, 1,1-dlphenyl ethylene and cycloctene. and acetylenes such as 1-pentyne and 1-octyne has been studied.

In addition, the decomposition in cycloctene has been investigated in detail.

INTRODUCTION

Catalytically, thermally and photochemically induced decompositions of diazocompounds are well known¹⁻⁵ processes which yield carbenes and carbenoids. It is generally recognised that singlet carbene is formed in direct irradiation, as triplet carbene formation is predominant In sensitized irradiation. Singlet Carbenes act as electrophiles in addition reactions and stereospecific addition occurs by a synchronous mechanism. On the other hand, triplet carbenes give non-stereospecific additions via two-step mechanism (equation 1 and 2).

Beside addition reactions, insertion of carbenes to present C-H bond may occur, even if, with less probability. Tendency to these reactions increases with the reactivity of the carbenes. We have used dimethoxycarbonyl carbene throughout the work. Replacement of hydrogens of methylene carbene ($:HC_S$), which is the most basic carbene, with bis-alkoxycarbonyl leads to the formation of more stable carbene (less reactive but more selective). Thus, dialkoxycarbonylcarben prefers insertion to the tertiary C-H bond*. This selectivity may be due to a contribution to the transition state from dipolar,structures, tertiary carbon being able to carry positive charge better than the primary (eq. 3).



Addition to acetylenes occurs less readily than olefins. This can be explained by the decreasing nucleophilic character of carbon-carbon triple bond and unstability of formed cyclopropenes⁴. Alkyl substitution increases the stability of cyclopropenes.

The formation of furan derivatives instead of cyclopropene derivatives were observed under specific circumstances⁷⁸

EXPERIMENTAL

Materials

Dimethyldiazomalonate was prepared as described previously⁹.

All of the olefins and acetylenes (from Fluka) were used as purchased.

Spectroscopic and Gas Chromatographic Studies

Infrared spectra were measured on a Shimadzu IR-4CO model spectrometre. NMR spectra were measured on a Varian Associates T-60 instrument using TMS as an external standart. Gas Chromatographic studies were performed on a Shimadzu instrument model 5A with flame ionization detection using the column 3m, 3% OV-17 on AW, DMCS chromosorb W 60/80 mesh.

Photolysis Studies

General

Appropriate solutions of olefins or acetylenes and dimethyldiazomalonate were placed in a double walled, water cooled immersion well photoreactor. 125 watt medium pressure mercury lamp was used as irradiation source through pyrex vessel.

Only when 2,4,4-trimethyl-2-pentene was employed as olefin, photolysis was performed on a similar reaction mixture contained in a pyrex vessel with the twofifteenth mercury lamp maintained below 20°C and unfiltered irrerrcliffton from a 250 watt- medium presurre mercury lamp.

All of the photolysis were carried out under nitrogen and photolysis times were chosen so as to permit complete decomposition of dimethyldiazomalonate.

a — Photolysis of DMDM In 1-pentyne

A solution of 804.1 mg DMDM in 50 ml 1-pentyne was irradiated for 21 hours. After vacuum distillation of excess acetylene the yellow residue was analysed by Gas Chromatography. Two major products 83% I and 30.5% II were revealed.

IR: 1736 (s, carbonyl), 3880 (m, acetylenic C-H), 3.150 (m, cyclopropenyl C-H)^{10,11} 2150 (m, acetylenic C=C). 1840 cm⁻¹ (w cyclopropenyl C=C)¹².

NMR: δ 6.23 (s, 1H cyclopropenyl p.H, 3.6 (s, 6H, ester p.) identified I as 1-n-propyl-3,3-dimethoxycarbonylcyclopropene. In addition to I 3.73 (s, 6H, ester p.); 3.2 (1H malonyl p.) signals showed H as dimethyl -(1-ethynyl) isopropyl malonate.

b — Photolysis of DMDM In 1-octyne.

A solution of 548.5 mg DMDM In 50 ml. 1-octyne was irradiated for 20 hours. After vacuum distillation of excess acetylene the yellow residue was analysed by Gas Chromatography. One main product 82% III was detected.

IR: 1737 (s, carbonyl), 3140 (m, cyclopropenyl C-H), 1840 cm⁻¹ (w, cyclopropene C=C).

NMR: δ 6.24 (d, 1H, cyclopropenyl), 3.6 (s, 6H, ester p.) Identified III as 1-n-hexyl-3,3-dimethoxycarbonylcyclopropene.

c — Photolysis of DMDM in 2,4,4-trimethyl-2-pentene

A solution of 316 mg DMDM in 31.128 ml olefin was irradiated for 23 hours as described in general section. After vacuum distillation of excess olefin, the residue was analysed by Gas Chromatography. Three major products 22.5% IV, 18.2% V, and 17.9% VI were shown.

IR: 1720 (s, carbonyl), 1646 cm⁻¹ (m, C=C). NMR: δ 4.7 (vinyl p.) and 3.8 (ester p.)

Beside residual olefin and starting materials all of the theoretically possible three products were formed in this reaction.

d — Photolysis of DMDM In 1,1-diphenylethylene

A solution of 448.7 mg DMDM in 10 ml olefin was irradiated for 22 hour. We were unable to analyse the residue by Gas Chromatography due to the lack of proper column.

However, IR: 1740 cm⁻¹ (s, carbonyl) and NMR: δ 7-15 (s, aromatic p), 5.24 (s, vinyl p.), 3.22 (s, ester p.), 2.2 (ring p.) Indicated VII but with some evidence for varying, but small, residual amount of starting olefin.

e — Photolysis of DMDM in Cycloctene

A solution of 3.655 g DMDM in 75 ml olefin was irradiated for 23 hours. Samples taken from the photolysis solution at given times were analysed by IR and GC. At the end of the reaction, the excess olefin was vacuum distilled and Gas Chromatographic analysis showed one major product as VIH.

IR: 1725 (s. carbonyl), 3000-2850 (s, C-H str.) 1460-1440 cm^{-1} s. C-H vib) Compound VIII was identified with aid of IR spectra of the available standard.

RESULTS AND DISCUSSION

We have undertaken studies on the kinetic behaviour of the photolysis of DMDM for this purpose, cycloctene was chosen as a model compound, since the relevant feature of the reaction when catalytical conditions employed, was available⁷. The reaction mixture was irradiated and samples were taken from the solution at given times. The consumption of DMDM was calculated between each irradiation from IR spectra at 2130cm^{-1} which corresponds to the azo band¹⁴ (Fig. 1 and 2),

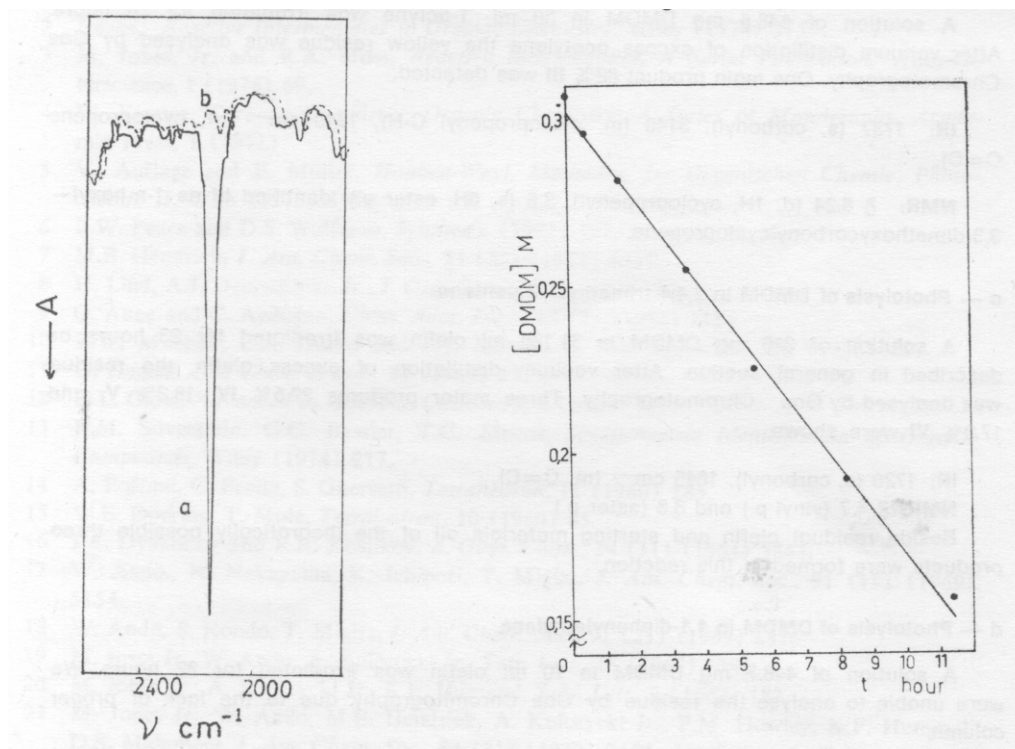
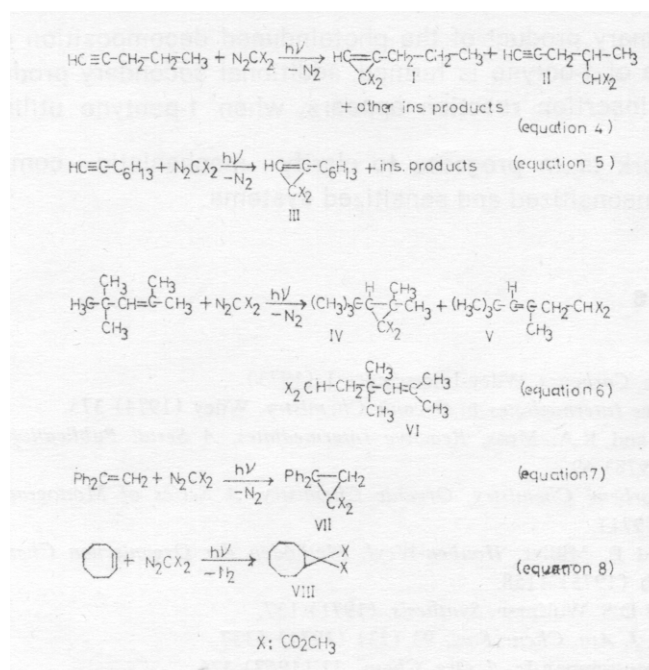


FIGURE 1. Infrared spectral change of DMDM in cycloctene, a) Before irradiation, b) After 23 hours irradiation.

FIGURE 8. Consumption of DMDM in cycloctene during irradiation.

Although there has been growth of interest^{15,21} on the photolytic formation and reactions of carbenes, no work on the photolysis of DMDM in 1-octyne, 1-pentyne and 2,4,4-trimethyl-2-pentene, 1,1-diphenylethylene and cycloctene has been reported. Such a choice is justified by a clear interpretation of the product analysis which will be dealt later in the paper. In the light of present knowledge, following equations may be represented indicating photochemical cycloaddition and Insertion reactions.



Fortunately, In all cases, the completion of the reaction was observed by the disappearance of the strong azo band in IR spectra. The number of products and yield were detected by G.C. Then, the structures of the products can be proven by spectral analysis with emphasis on ¹H-NMR- if the number and percentage of the compounds are known.

The most important point to note is that the absence of signals in the region associated with vinyl proton when studied with olefins and the appearance of cyclopropenyl proton near δ 7 instead of acetylenic proton near δ 1.7, in the case of acetylenes. Because of above considerations, monosubstituted acetylene derivatives have been chosen for our work, since there would be no detectable cyclopropenyl proton by ¹H-NMR in the addition product of disubstituted acetylenes. Similarly, olefins containing at least one vinyl proton deliberately used so as to permit spectral detection.

Addition to tetra-substituted olefins can be succeeded only with low yields- due to the steric hinderance. Therefore, in the photolysis of DMDM in 2,4,4-trimethylpentene, all possible products were shown to be present in the reaction mixture.

Aromatic ring and vinyl protons are responsible for the only addition product of 1,1-diphenylethylene⁶.

As the primary product of the photoinduced decomposition of DMDM in the presence of 1-octyne is formed, additional secondary product which resulted from insertion reaction appears, when 1-pentyne utilised.

Further work is in progress to clarify mechanistic complications exist for both unsensitized and sensitized systems.

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