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The Photolysis of Dimethyl Diazomalonate in Alcohols. The Detection of Triplet Carbene

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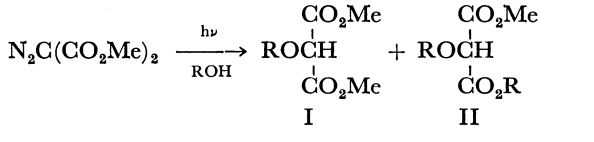
Synopsis. The photolysis of dimethyl diazomalonate n alcohols gave the O–H insertion product of biscarbomethoxycarbene and dimethyl malonate as the major products. The dimethyl malonate might be formed by the hydrogen abstraction of a triplet carbene.

There have been a few reports which show the occurrence of a triplet carbene in the direct photolysis of diazo compounds, whereas its benzophenone-sensitized photolysis is generally accepted to produce a triplet carbene.[1,2]

This paper will report some examples in which substantial amounts of hydrogen abstraction from alcoholic solvents and of non-stereospecific addition to olefin result from the biscarbomethoxycarbene produced through the photolysis of dimethyl diazomalonate in alcoholic media.

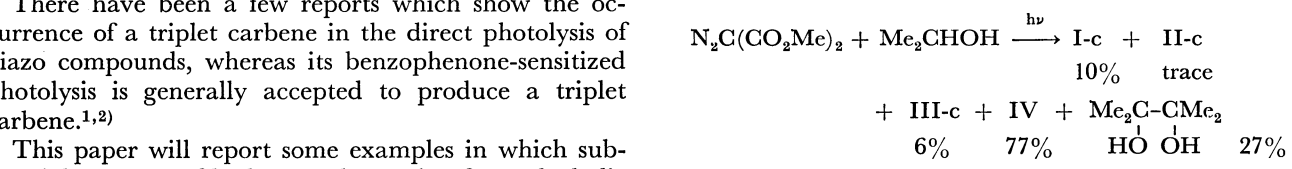
The direct irradiation of a methanol solution of dimethyl diazomalonate (0.16 g in 2.5 ml) was carried out with a high-pressure mercury lamp until the disappearance of the diazo compound. A gas chromatographic analysis of the reaction mixture gave dimethyl methoxymalonate and dimethyl malonate in 78 and 10% yields respectively; the structures of the products were established by NMR, IR, and elemental analyses. Appropriate control experiments showed that the products are stable under the present reaction conditions.

The photolysis in ethanol gave four products; dimethyl ethoxymalonate (I-b), ethyl methyl ethoxymalonate (II-b), ethyl methyl methoxymalonate (III-b), and dimethyl malonate (IV). From the photolysis of the diazomalonate in 2-propanol, the Wolff rearrangement product (III) was obtained together with the O–H insertion (I) and ester exchange (II) products, as minor products, while dimethyl malonate became the major product.



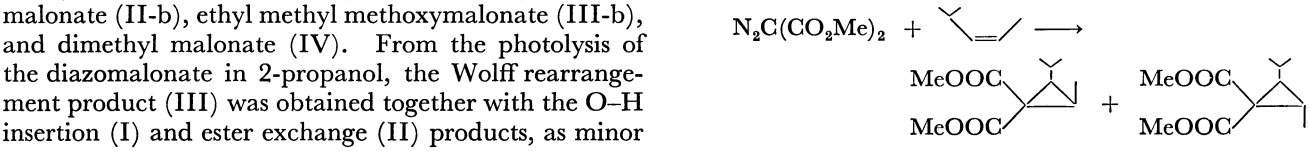
		I	II	III	IV
a	R=Me	78%	—	—	10%
b	R=Et	33	2%	13%	34
c	R=*iso*-Pr	21	4	12	41
d	R=*tert*-Bu	40	5	12	0

It is noteworthy that the photolysis of diazomalonate produced substantial amounts of dimethyl malonate, which increased with an increase of the H-donor abilities of the alcohols. Furthermore, a change of the concentration of the diazomalonate from 1 mmol to 0.2 mmol in 5 ml 2-propanol resulted in an increase in the yield of dimethyl malonate from 41 to 77%, with the formation of pinacol (27%) and the O–H insertion product (10%).



Although I and III are quite familiar products of the reaction of the singlet carbene derived from the diazo compound in alcohols,[3,4] the formation of malonate and pinacol can be though to be rather characteristic for the triplet carbene, which can abstract the α-hydrogen atom from alcohol. Indeed, the benzophenone-sensitized photodecomposition of dimethyl diazomalonate in ethanol and 2-propanol gave dimethyl malonate in 74—80% yields.

It is also worth noting that the photolysis of diazomalonate in mixtures of *cis*-4-methyl-2-pentene and alcohols gave cyclopropane derivatives in a non-stereospecific manner, but rather similar to the case of the photosensitized reaction,[5] especially in the presence of methanol, although the total yields of the adducts were quite low.



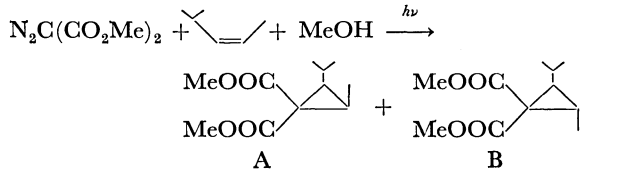
hν	92%	8%
hν + Ph_2C=O	14%	86%
hν + MeOH[a]	18%	82%
hν + EtOH[a]	66%	34%
hν + *iso*-PrOH[a]	75%	25%

a) The mole ratio of *cis*-4-methyl-2-pentene and alcohol is 1 : 10.

These findings strongly support the idea that the triplet species are involved in the direct photolysis of diazomalonate in alcohols. Singlet carbene reacts with alcohols to give either O–H insertion or Wolff-rearrangement products, while the residual carbene, which contains the triplet, abundantly reacts with olefin to give non-stereospecific adducts.

At present, the occurrence of the triplet carbene in the direct photolysis of diazomalonate in alcohols is thought to be brought about through some intersystem crossing processes. The small amounts of triplet carbene thus formed abstract a hydrogen atom from

Table 1. Reaction of dimethyl diazomalonate with *cis*-4-methyl-2-pentene in methanol



Mole ratio MeOH/	Product ratio, % A	B
1	63%	37%
2	42	58
4	38	62
10	18	82

alcohol, and the α-hydroxalkyl radical may induce the decomposition of diazomalonate by chain processes, giving substantial amounts of dimethyl malonate, since the thermal decomposition of diazomalonate in the presence of benzoyl peroxide in alcohol has been known to give dimethyl malonate in a good yield.[6]

Experimental

General. Solutions of dimethyl diazomalonate were placed in clean 10×100 mm Pyrex tubes. The tubes were corked (non-degassed), placed in a water-cooled bath, and then irradiated by means of a Rikosha 400-W high-pressure mercury lamp, with a maximum output at 3650—3660 Å. Photolyses were carried out until the diazo band in the infrared region disappeared. The solutions were analyzed on an Ohkura gas chromatograph with a calibrated 2 m×4 mm stainless steel column of 15% silicon SF-96 on Celite 545. The products were characterized by NMR (see the table shown below), IR and elemental analyses.

Reaction of Dimethyl Diazomalonate with Methanol. A solution of 187 mg of dimethyl diazomalonate in 1 ml of methanol was cooled with running water and irradiated through Pyrex with a high-pressure mercury lamp for 5 hr. After the distillation of the solvent, the residue was fractionated by gas chromatography. The major product was then collected. I-a: Found: C, 44.15; H, 6.02%. Calcd for $C_6H_{10}O_5$: C, 44.44; H, 6.22%.

Reaction of Dimethyl Diazomalonate with Ethanol. A solution of 155 mg of dimethyl diazomalonate in 1 ml of ethanol was similarly irradiated for 3 hr. Subsequent gas chromatography gave 34% of dimethyl malonate and 33% of a major product identified as dimethyl ethoxymalonate(I-b). The minor products were collected in 2% (II-b) and 13% (III-b) yields. I-b: Found: C, 47.58; H, 6.93%. Calcd for $C_7H_{12}O_5$: C, 47.72; H, 6.87%. II-b: Found: C, 50.29; H, 7.18%. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42%. III-b: Found: C, 47.86; H, 6.75%. Calcd for $C_7H_{12}O_5$: C, 47.72; H, 6.87%.

Reaction of Dimethyl Diazomalonate with 2-Propanol. Irradiation of a solution of 160 mg of dimethyl diazomalonate in 1 ml of 2-propanol gave I-c and IV as major products, and II-c and III-c as minor products. When a solution of 160 mg of dimethyl diazomalonate in 5 ml of 2-propanol was irradiated, the five products were isolated by gas chromatography at 160 °C. The two major products were pinacol (47% yield) and dimethyl malonate (64% yield). The minor products were found to to be I-c (8%), II-c (trace), and III-c (5%). I-c: Found: C, 50.43; H, 7.32%. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42%. II-c: Found: C, 54.93; H, 8.12%. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.21%. III-c: Found: C, 50.16; H, 7.39%. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42%.

Reaction of Dimethyl Diazomalonate with tert-*Butyl Alcohol.* A solution of 152 mg of dimethyl diazomalonate in 1 ml of *tert*-butyl alcohol was irradiated for 5 hr through Pyrex tubes. The products were analyzed by gas chromatography at 170 °C. The major product was identified as I-d by spectral analysis. The minor products were collected in 5% (II-d) and 12% (III-d) yields. I-d: Found: C, 52.45; H, 7.95%. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90%. II-d: Found: C, 58.37; H, 8.95%. Calcd for $C_{12}H_{22}O_5$: C, 58.51; H, 9.00%. III-d: Found: C, 52.78; H, 8.12%. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90%.

Sensitized Decomposition of Diazomalonate in Alcohols. A solution of 170 mg of dimethyl diazomalonate and 0.95 g of benzophenone in 2.5 ml of alcohol was placed in a Pyrex tube under a nitrogen atmosphere and irradiated with the high-pressure mercury lamp for 5 hr. Gas-chromatographic analysis gave only dimethyl malonate as a major product.

Decomposition of Dimethyl Diazomalonate in cis-*4-Methyl-2-pentene and Alcohols.* All the samples, in Pyrex tubes, were irradiated under nitrogen with the same light source for the same long time. The products were analyzed by gas chromatography. The results of a typical run, in which dimethyl diazomalonate and *cis*-4-methyl-2-pentene were dissolved in methanol, are shown in Table 1.

NMR Data of the Products

Compd	NMR spectrum in CCl_4 (ppm)
I-a	3.48(s, 3H), 3.08(s, 6H), 4.30(s, 1H).
I-b	1.28(t, 3H), 3.62(q, 2H), 3.76(s, 6H), 4.33(s, 1H).
II-b	1.28(t, 3H), 1.32(t, 3H), 3.63(q, 2H), 3.76(s, 3H), 4.22(q, 2H), 4.32(s, 1H).
III-b	1.30(t, 3H), 3.45(s, 3H), 3.74(s, 3H), 4.23(q, 2H), 4.26(s, 1H).
I-c	1.20(d, 6H), 3.4—3.8(m, 1H), 3.75(s, 6H), 4.38(s, 1H).
II-c	1.18(d, 6H), 1.26(d, 6H), 3.4—3.8(m, 1H), 3.73(s, 3H), 4.11(s, 1H), 4.8—5.3(m, 1H).
III-c	1.27(d, 6H), 3.44(s, 3H), 3.75(s, 3H), 4.20(s, 1H), 4.7—5.4(m, 1H).
I-d	1.20(s, 9H), 3.73(s, 6H), 4.45(s, 1H).
II-d	1.22(s, 9H), 1.45(s, 9H), 3.72(s, 3H), 4.31(s, 1H).
III-d	1.48(s, 9H), 3.45(s, 3H), 3.75(s, 3H), 4.14(s, 1H).

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