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The Reaction of Bis(methoxycarbonyl)carbene with Allyl Chloride. "Solvent Effect"

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We have recently reported that the bis(methoxycarbonyl)carbene generated by the photochemical decomposition of dimethyl diazomalonate reacts with allyl halides to give addition products to the carbon-carbon double bond, cyclopropane derivatives (I) and the carbon–halogen insertion product, allylhalogenomalonate (II).[1] We have also indicated that only singlet bis(methoxycarbonyl)carbene is capable of affording the insertion product through an allylic rearrangement of the halonium ylide intermediate, and that the triplet carbene produced by a benzophenone-photosensitized decomposition is added to olefin rather than interacts with the halogen atom.[2]

A carbene in a singlet excited state has been reported to be transformed into the triplet state by collision with inert solvents,[3,4] particularly with those possessing heavy atoms.[5] The effect of such a collisional transformation may be expected to affect the ratio of the insertion and the addition products if the reactions of bis(methoxycarbonyl)carbene with allyl halides are carried out in such solvents. In this paper, we wish to repot on the ratio of the insertion and the addition products in the photochemical reactions of dimethyl diazomalonate with allyl chloride in methylene halides and cyclohexane as the solvents, these data will give some evidence of transformation into the deactivated bis(methoxycarbonyl)carbene produced by the collision of singlet bis(methoxycarbonyl)carbene with solvent molecules. The results are compiled in Table 1.

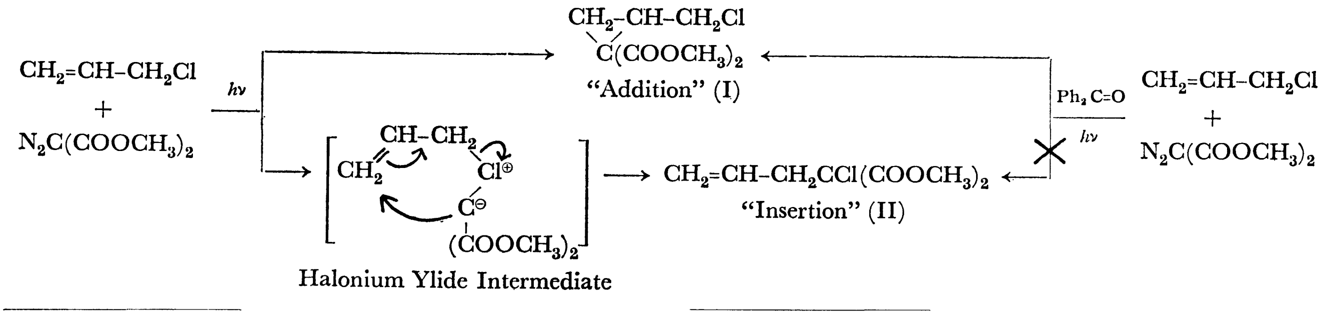
We can immediately see that the ratio of the insertion and addition products (II/I) decreases with dilution with methylene halides, and it tends toward the value obtained in the benzophenone-sensitized reaction. We take this to indicate that the reacting carbene species are partly triplet in these solvents and that almost they are exclusively triplet in the system highly diluted with CH_2Br_2. Furthermore, in 10% methylene halides, the ratio of the insertion and addition products is highest in CH_2Cl_2 and lowest in CH_2I_2. These tendencies are in agreement with the findings that the singlet-triplet interconversion is more effective when the reaction solvents possess heavier halogen atoms.[6] The overall yields (I+II) decreased as the concentration of methylene halides increased. This is probably because of the reaction of the singlet carbene with the solvent to give halogenomalonate as well as the insertion product into the carbon–halogen bond of the solvent.[7]

$$N_2C(CO_2CH_3)_2 + CH_2X_2 \xrightarrow{h\nu} CH_2XCX(CO_2CH_3)_2 + CHX(CO_2CH_3)_2$$

TABLE 1. THE EFFECTS OF SOLVENTS ON THE PHOTOCHEMICAL DECOMPOSITION OF DIMETHYL DIAZOMALONATE IN ALLYL CHLORIDE

Solvent	Concn.[a] %	II/I	Overall yield %
none	0	2.35	76
none+Ph_2C=O	0	0.056	93
C_6H_{12}	10	3.39	64
C_6H_{12}	50	2.52	26
C_6H_{12}	90	1.95	5
CH_2Cl_2	10	2.38	60
CH_2Cl_2	50	2.20	35
CH_2Cl_2	90	1.17	10
CH_2Br_2	10	2.19	36
CH_2Br_2	50	1.60	14
CH_2Br_2	90	0.06	4
CH_2I_2	10	1.94	27

a) Mole per cent of solvents.
b) Yield of a mixture of the insertion and the addition products based on used diazomalonate.



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Therefore, an alternative explanation might be advanced: perhaps the singlet carbene is trapped preferentially by the solvent, thus giving a higher proportion of the triplet in the solution and leading to more of the addition product. Unfortunately, the reaction mechanism of the carbene with methylene halides is not yet clear.

The addition of cyclohexane to the irradiation mixture results in initially increased yields of the insertion products. This can presumably be explained in terms of the deactivation of a part of the excited singlet carbenes formed by photolysis to the lowest singlet state in which it can react more selectively. A similar dilution effect has previously been reported, that is, dilution with hexafluorobenzene increased the stereospecificity of the addition of bis(methoxycarbonyl)carbene to a olefin.[8]

On the basis of the data presented here, we may conclude that the singlet carbene formed by the photolysis of dimethyl diazomalonate can be readily deactivated, through collisions with methylene halides, to the triplet carbene, which is incapable of ylide formation with allyl chlorides.

Experimental

General. Samples of dimethyl diazomalonate were placed in clean 10×100 mm Pyrex tubes. The tubes were then corked(nondegassed) and placed in a water-cooled bath in order to irradiate them. The light source was a Rikosha 400-W high-pressure mercury lamp with maximum out-put at 3650—3660Å. Photolyses were carried out until the diazo band in the infrared spectra disappeared. The solutions were analyzed on an Ohkura gas-liquid partition chromatography with a calibrated 2 m×4 mm stainless steel column of 10% DC-710 and 10% Carbowax 20M on C-22 Firebrick.

Preparation of Dimethyl Diazomalonate. A solution of dimethyl diazomalonate(26.4 g) and tosyl azide (39.4 g) in diethyl ether (200 m*l*) was treated at 0°C with dry diethylamine (20 m*l*). The mixture was stirred for 1 hr at 0°C, and then for a further hour at room temperature. When a solid has been deposited, the mixture was treated with petroleum ether (bp below 60°C) and the solid was filtered off. The removal of solvent from the filtrate and the distillation of the residue gave dimethyl diazomalonate; bp 60—61°C/2mmHg (50% yield), (lit,[9] 63°C/1 mmHg).

Reaction of Dimethyl Diazomalonate in Allyl Choride. In a typical run, 0.218 g (0.0013 mol) of diazomalonate in 1 m*l* of allyl chloride was irraidated in a Pyrex tube for 5 hrs. Dimethyl allylchloromalonate and bis(methoxycarbonyl)cyclopropane were observed as the major products in yields of 53 and 23% respectively. Dimethyl allylchloromalonate showed infrared bands at 1752, 1645, and 950 cm^{-1}, and its NMR spectrum showed at 1.92 (doublet, 2-H), 3.78 (singlet, 6-H), and 5.24 ppm(multiplet, 3-H). Found: C, 46.71; H, 5.49%. Calcd for $C_8H_{11}O_4Cl$: C, 46.48; H, 5.32%.

The cyclopropane showed an infrared band at 1725 cm^{-1}, and its NMR spectrum showed bands at 1.43 (doublet, 1-H), 1.55 (singlet, 1-H), 2.12 (multiplet, 1-H), 3.50 (doublet, 2-H), 3.71 (singlet, 3-H), and 3.75 ppm (singlet, 3-H). Found: C, 46.49; H, 5.43%. Calcd for $C_8H_{11}O_4Cl$: C, 46.48; H, 5.32%.

Photosensitized Decomposition of Dimethyl Diazomalonate in Allyl Chloride. A solution of 0.325 g of diazomalonate and 1.74 g of benzophenone was irradiated in 2 m*l* of allyl chloride. The usual work-up yielded 88% of bis(methoxycarbonyl)-cyclopropane and 5% of the insertion product, dimethyl allylchloromalonate.

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