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MECHANISMS OF THE PHOTOCHEMICAL REACTION OF DIMETHYL DIAZOMALONATE WITH CYCLOHEXENE AND METHYLCYCLOHEXENE AS A FUNCTION OF TEMPERATURE[1]

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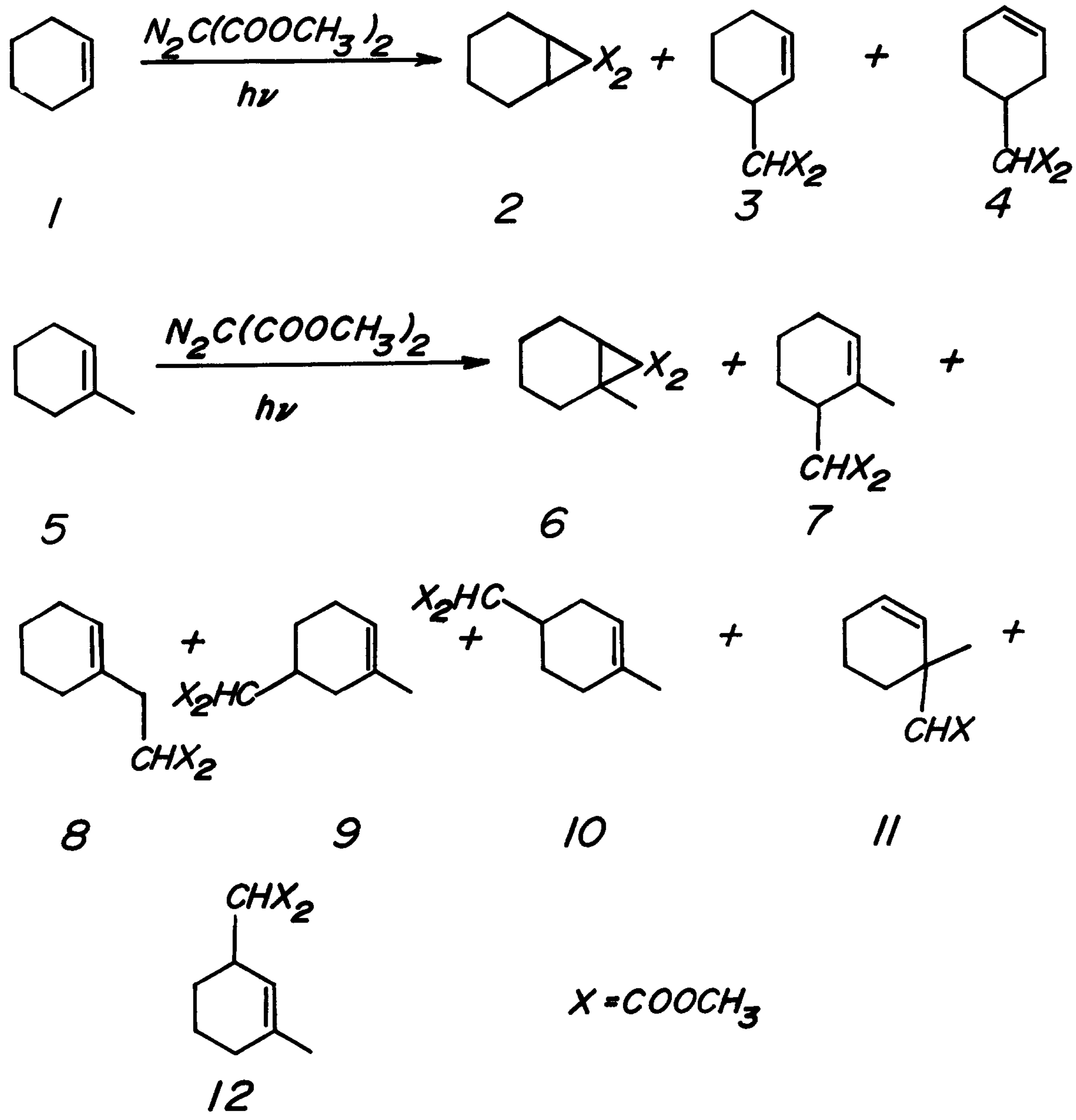
The assumption that the reactive intermediate during the metal salt catalyzed cyclopropanation of olefins by diazo alkanes is a carbene metal complex (carbenoid) rests upon two fundamental facts 1) differences between the processes obtained catalytically and photochemically[2]; 2) optical inductions in the presence of chiral catalysts[3]. The existence of free carbenes during photolyses of diazo alkanes rests by analogy upon a few well studied photolyses of some not necessarily representative diazo alkanes, eg. diazomethane[4]. Kirmse[5] has stated that "The long lasting fascination of the carbene concept for organic chemists appears to have emotional rather than empirical grounds." One can explain the photochemical and catalytic reactions of diazo alkanes without invoking carbene or carbenoid intermediates[5,6]. It is known that the reactivities of diazo acetic esters and diazo malonic esters are different in their modes of decomposition (photolytic vs catalytic)[8,9,10]. We have tried to establish the existence of bis-methoxycarbonyl carbenoids by analyzing the activation parameters for both catalytic and photolytic processes but the data in the Table casts strong doubt as to the existence of free carbenes during the cyclopropanation of olefins and during insertions into the allylic CH bonds by the alleged singlet carbene. It is clear that although the rate of reaction is dependent upon the number of photons available, the thermochemical rate determining step occurs after the photochemical processes and involves the substrate olefin.

From the data it is evident that products 2 and 3 arise from a common intermediate and that 4 is derived from a different intermediate. It is equally clear that 2 and 6 arise from different intermediates. The value of $\delta\Delta G^*$ for the generation of 2 and 6 is rather high for a process involving a high energy carbene.

There are two simple explanations 1) a charge transfer complex is formed between the olefin and the carbene, or; 2) the photoexcited diazo compound forms a complex which then proceeds to the final products. The fact that the formation of 4 has a $\delta\Delta G^*$ higher than that



$N_2C(COOCH_3)_2$
$h\nu$
X_2
CHX_2
1
2
3
4
$N_2C(COOCH_3)_2$
$h\nu$
X_2
CHX_2
5
6
7
CHX_2
X_2HC
X_2HC
CHX
8
9
10
11
CHX_2
12
$X = COOCH_3$

TEMPERATURE °C	RATIO 3:2	$\delta\Delta G^{\ddagger}$ Kcal.mol.$^{-1}$	RATIO 4:2	$\delta\Delta G^{\ddagger}$ Kcal.mol.$^{-1}$	RATIO 2:6	$\delta\Delta G^{\ddagger}$ Kcal.mol.$^{-1}$	CONDITION
0	0.47		0.05				PURE
54	0.46		0.11	2.6			
0	0.46		0.23				90 mole % C_6F_6
54	0.47		0.39	1.7			
0	0.13		0.11				$(C_6H_5)_2CO$ SENS
54	0.19	1.1	0.10				
35					0.33		compounds1+5 in ratio 1:1
90					0.909	4.0	

for cyclopropanation (≈ 2.1 to ≈ 1.7 kcal.) is consistent with these hypotheses. The triplet carbene envisaged as forming 3 and 4 in the sensitized reaction furnished $\delta\Delta G^*$ values of ≈ 1.1 and 0.0 kcal. Thus the alleged singlet carbene which is supposed to react in a concerted fashion has higher activation parameter differences than the alleged triplet process which is thought to proceed in a non-concerted manner.

We are therefore forced to conclude that a free singlet carbene is not an intermediate during the non-sensitized photolysis of dimethyl diazomalonate. One can envisage: 1) for the formation of the cyclopropanes and the allylic C-H insertion products (a) the photo-excited diazo compound forming a complex with the olefine, or (b) the excited diazo compound forming an excited pyrazoline, 2) for the formation of non-allylic C-H insertion products (a) direct attack by photo-excited diazo compound, or (b) a free carbene. We prefer the (a) interpretations because the P-N_2 process does not occur in the mass spectrometer (9 ev to 110 ev)[11] and the diazo compound does not lose N_2 readily even in refluxing cyclohexene. In addition it is well known that the loss of nitrogen from the readily fragmented diazo compound, diazomethane is reversible[12,#]. This problem is under further study.

Bibliography and Notes

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3) W. Kirmse, loc. cit., Chapter 3, see also reference 1.
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6) For example one might envisage the photo-excited diazo alkane as a very strong 1,3 dipole or as a biradical.
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\# A modest stability of diazo alkanes to photochemical loss of N_2 has been demonstrated with the photochemical isomerization of a number of heterocycles to related diazo compounds (cf. Kirmse Chapter 2).

γ Clean separations upon gas chromatography of the isomers 7-12 were not realized.