

THE ADDITION OF BIS-CARBOMETHOXYCARBENE TO OLEFINS (1)

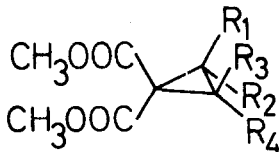
Maitland Jones, Jr., Anthony Kulczycki, Jr., and Karl F. Hummel

Department of Chemistry, Princeton University

Princeton, New Jersey 08540

(Received 21 September 1966)

Photochemical decomposition of diazomalonate esters is known to yield bis-carboalkoxycarbenes (2). While the reaction of such carbenes with the carbon-hydrogen bond has been studied (2), there seems to be no report of the photochemically induced addition to olefins. We wish to describe such additions and the further properties of bis-carbomethoxycarbene (1).



II, R₁=R₃=H; R₂=CH₃; R₄=CH(CH₃)₂

V, R₁=R₄=H; R₂=R₃=CH₃

III, R₁=R₄=H; R₂=CH₃; R₃=CH(CH₃)₂

VI, R₁=H; R₂=R₃=R₄=CH₃

IV, R₁=R₃=H; R₂=R₄=CH₃

VII, R₁=R₂=R₃=R₄=CH₃

Irradiation of solutions of dimethyl diazomalonate in olefins leads to 1,1-dicarbomethoxycyclopropanes in moderate yield (Table 1). Photolysis was carried out in Pyrex vessels with General Electric Sunlamps as the light source in order to avoid possible photoisomerization of the expected adducts.

TABLE 1

Olefin	Product	Yield of Cyclopropane	Yield of Other Products (%)
<u>cis</u> -4-methyl-2-pentene	II	59.8	5.4
<u>trans</u> -4-methyl-2-pentene	III	24.5	7.5
<u>cis</u> -2-butene	IV	23.4	---
<u>trans</u> -2-butene	V	16.3	4.8
2-methyl-2-butene	VI	43.0	6.0
2,3-dimethyl-2-butene	VII	28.0	10.7

More interesting than such additions which by now must surely be regarded as commonplace, are the results of investigations of the selectivity of I and of the stereochemical course of the reaction. In order to gain some measure of the selectivity of I, dimethyl diazomalonate was irradiated in pairs of olefins. Table 2 compares the relative rates of addition to various olefins of I and several other carbenes. In all cases the thermal conductivity detector was calibrated for the different addition products. The data indicate that I as well as carbalkoxycarbene (4) cyclopentadienylidene (5) and 2,2-diphenylcyclopropylidene (6) is rather more sensitive to steric effects than electronic. The addition still seems to be electrophilic, but steric factors are dominant.

In an attempt to observe intersystem crossing from the initially produced singlet to the presumably more stable triplet we have monitored the stereochemistry of the products of addition of I to cis olefins as a function of added inert medium. As previously (8), hexafluorobenzene was used as the inert diluent. By the criterion of Skell (9) the triplet state would be expected to add non-stereospecifically to the cis olefin to yield both cis and trans cyclopropane. That the triplet state of I does

TABLE 2

Olefin	I	Relative Rate		
		:CHCOOR ^a	Cyclopenta- dienylidene ^b	:CCl ₂ ^c
2,3-dimethyl-2-butene	0.88	1	1	2.3
2-methyl-2-butene	1	1	1	1
cyclohexene	-	0.62	1.3	0.04
1-hexene	-	-	1.25	0.008
1-pentene	0.47	0.55	-	0.002
3,3-dimethyl-1-butene	0.48	-	0.93	-
<u>cis</u> -4-methyl-2-pentene	0.55	-	-	0.02 ^d
<u>trans</u> -4-methyl-2-pentene	0.23	-	-	0.01 ^d
styrene	-	-	1.25	-
2,3-dimethyl-1,3-butadiene	1.31	-	-	-

^aData of Skell and Etter (4) ^bData of Moss (5) ^cData of Doering and Henderson (7) ^dM. Jones, Jr., Unpublished Work.

indeed add non-stereospecifically was shown by the benzophenone photo-sensitized (10) decomposition of diazomalonic ester (Table 3).

TABLE 3

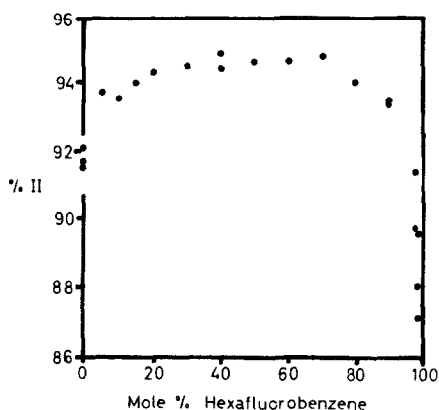
Irradiation of Methyl diazomalonate in cis-4-Methyl-2-pentene

Conditions	%II	%III	Total Yield of Cyclopropanes
(CH ₃ OOC) ₂ CN ₂ + hν	92	8	39.8
(CH ₃ OOC) ₂ CN ₂ + Ph ₂ CO + hν	15	85	43

Intersystem crossing seems to be much more difficult for I than for fluorenylidene (8). Only after large amounts of hexafluorobenzene have been added does the amount of trans cyclopropane (III) increase. Indeed, the amount of cis cyclopropane (II) increases initially, reaches a broad maximum at ca. 50% hexafluorobenzene concentration, then finally declines. Apparently there are two sources of trans product, each dependent upon moderator concentration in a different way. Similar results are obtained in the addition to cis-2-butene. Solvent olefin is not isomerized under these conditions.

FIG. 1

Reaction of I with cis-4-Methyl-2-pentene and Hexafluorobenzene



We feel that the final decline in the amount of cis product is due to the intervention of triplet I. While the magnitude of the change observed is small, the direction is clear and the explanation offered seems probable. The initial increase is even more difficult to explain. It has been demonstrated that some carbene precursors are able to undergo intersystem crossing before decomposing to carbenes. (12-14)

Thus excited diazo compounds must be included as potential reactive intermediates in any mechanistic scheme. Were an excited diazo compound to add to the solvent olefin to form a pyrazoline, trans cyclopropane could result from a lack of stereospecificity in either the formation or decomposition step. Added hexafluorobenzene would allow the excited diazo compound more time in which to lose nitrogen thus decreasing the amount of trans cyclopropane formed by this route.

Hoffmann (15) has calculated that the first excited singlet state of methylene should add in a non-stereospecific manner to olefins. Should a similar intermediate be produced on irradiation of dimethyl diazomalonate addition of hexafluorobenzene would allow for increased deactivation to the lowest singlet state which should be stereospecific in its addition to olefins. Thus the observed initial increase in amount of cis cyclopropane would be observed.

REFERENCES AND NOTES

- (1) We gratefully acknowledge the generous support of the National Science Foundation in the form of grant NSF-GP-5257 and two National Science Foundation Undergraduate Participation Fellowships to one of us (A.K.). We further acknowledge the most helpful support of the Lilly Research Laboratories and illuminating discussions with Professor W. von E. Doering of Yale University.
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- (3) In large part, at least, these are products of carbon-hydrogen insertion into the allylic carbon-hydrogen bonds.
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