

importance of the term $2 \log (\bar{V}_{\text{ret}}/\bar{V}_s)$ in the variable X ; no corresponding solvent volume term is included in eq 1.

The value $\alpha = 0.93$ indicates that the free energy of solvation of pyridine $\cdot I_2$ is only slightly less than the sum of the free energies of solvation of the uncomplexed pyridine and I_2 molecules. Values of α in the range 0.7–0.8 have been calculated for relatively weak 1:1 hydrogen-bonded complexes,⁴ whereas the value $\alpha = 1.30$ has been reported for the strong 1:1 charge-transfer complex between SO_2 and trimethylamine (TMA).⁵ It has been proposed that the large dipole moment of TMA $\cdot SO_2$ (compared to the vector sum of the moments of TMA and SO_2) is responsible for the abnormally large free energy and energy of solvation of the complex and the corresponding large value of α .⁵ Apparently dipole enhancement is insufficient in pyridine $\cdot I_2$ to overcome the loss (in magnitude) of solvation free energy that occurs when the solvated D and A molecules are brought together to form the solvated complex.

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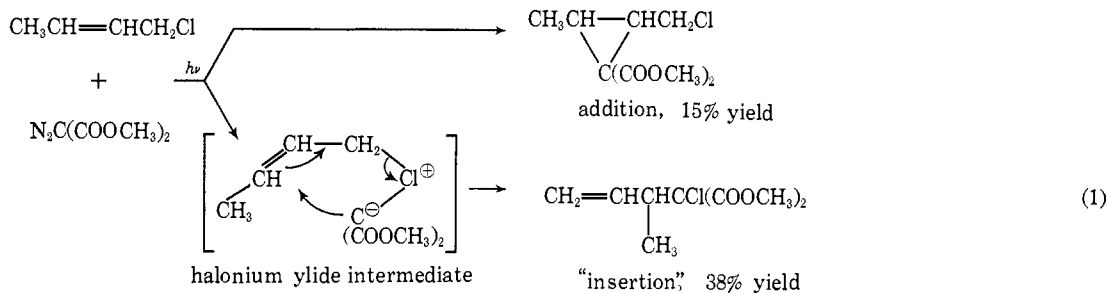
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Reactions of Carbalkoxycarbenes with Allyl Halides. Halonium Ylide Intermediates

Sir:

We previously reported that with dialkyl sulfides singlet carbalkoxycarbene directly attacks the unshared electrons on the sulfur atom to form alkylsulfonium ylides, but triplet carbalkoxycarbene cannot interact with unshared electrons on the sulfur atom and does not form the ylide.^{1,2}

We extended the studies on the reactions of carbenes with unshared electrons to the halides. The reactions



of allyl halides with carbenes have been studied by several workers,^{3,4} but there seems to be no report on the reaction with carbenes produced by photochemical, especially by photosensitized, reactions.

In this communication we wish to present the direct and photosensitized decomposition of diazocarbonyl compounds in allyl halides. Irradiation of a solution

of dimethyl diazomalonate in an allyl halide was carried out in a Pyrex vessel with a high-pressure mercury lamp.⁵ The reaction mixture was analyzed by vapor phase chromatography, and the structures of the isolated products were determined by nmr and ir spectra and elemental analysis.

The direct photolysis of dimethyl diazomalonate yields a singlet bis(carbomethoxy)carbene (I) which reacts with allyl chloride to give 53% of allyl chloromalonate and 23% of the cyclopropane derivative.

Table I. The Photolysis of Diazocarbonyl Compounds in Allyl Halides

Diazo compd	Halide	Insertion, ^c %	Addition, ^d %
DM ^e	CH ₂ =CHCH ₂ Cl	53	23
DM	CH ₂ =C(CH ₃)CH ₂ Cl	25	22
DM	CH ₃ CH=CHCH ₂ Cl	38 ^e	15
DM	CH ₂ =CHCH ₂ Br ^h	38	6
DA ^b	CH ₂ =CHCH ₂ Cl	21	18 ^f
DA	CH ₃ CH=CHCH ₂ Cl	15 ^e	7 ^f

^a Dimethyl diazomalonate. ^b Ethyl diazoacetate. ^c Allyl halide insertion product. ^d Olefin double bond addition. ^e α -Methylallyl chloromalonate. ^f Mixtures of *cis*- and *trans*-cyclopropanes. ^g Mixtures of α - and γ -methylallyl chloroethylacetate. ^h 37% of dimethyl bromomalonate was also obtained. Under the reaction conditions, the insertion product was unstable.

With γ -methylallyl chloride the formation of α -methylallyl chloromalonate and the cyclopropane were observed, but no γ -methylallyl chloromalonate was obtained.⁶ The formation of "insertion" products may be explained by the formation of halonium ylide followed by intramolecular allylic rearrangement (eq 1), as in the case of the reaction of bis(carbomethoxy)carbene with allyl sulfide or in the rearrangement of allylic sulfonium and ammonium ylides.^{2,7–10} With allyl bromide, an excellent yield was obtained by the "insertion" of bis(carbomethoxy)carbene into the carbon–bromine bond, whereas only a trace of addition product was

formed. In the reaction of bis(carbomethoxy)carbene with *trans*-1,4-dichloro-2-butene, the ratio of "insertion" to addition was about twice that obtained with allyl chloride, as is expected from the number of reactive chlorine atoms in the former substrate.

The most marked change in going from the direct photolysis to the sensitized one is in the ratio of the "in-

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sertion" and addition products produced by the reaction of the carbalkoxycarbene with allyl chlorides. The benzophenone-sensitized photodecomposition of dimethyl diazomalonate in allyl chloride resulted in 88% addition and a trace of "insertion" product (see Table II).

Table II. Benzophenone-Sensitized Decomposition of Diazo-carbonyl Compounds in Allyl Halides

Diazo compd	Halide	Insertion, ^d %	Addi-tion, ^e %
DM ^a	CH ₂ =CHCH ₂ Cl	5	88
DM	CH ₂ =C(CH ₃)CH ₂ CH ₂ Cl	Trace	86
DM	CH ₃ CH=CHCH ₂ Cl	Trace	49
DM	CH ₂ =CHCH ₂ Br ^f	4	30
DA ^{b,c}	CH ₃ =CHCH ₂ Cl	7	69
DA	CH ₂ =C(CH ₃)CH ₂ Cl	6	85
DA	CH ₃ CH=CHCH ₂ Cl	3 ^g	22

^a Dimethyl diazomalonate. ^b Ethyl diazoacetate. ^c Direct absorption of light by ethyl diazoacetate itself could not be completely neglected. ^d Allyl halide insertion product. ^e Olefin double bond addition. ^f 35% of dimethyl bromomalonate was also obtained. ^g Mixtures of α - and γ -methylallyl chloroethylacetate.

The attractive mechanism (eq 1) for the "insertion" product through the halonium ylide intermediate may be supported by the following evidence. In direct photolysis, the "insertion" reaction with allyl chloride was about 1~2.5 times faster than the addition, whereas with allyl bromide it was about 8 times faster than addition.¹¹ Since the reactivities of the double bonds toward the attacking carbene species are not considered to be very different in these two allylic substrates, the change in the ratio of "insertion" to addition may be due to the difference in nucleophilicity between a chlorine and a bromine atom. This consideration is supported by the results which were obtained by competitive experiments using pairs of allylic compounds.

Table III compares the relative rates of "insertion" and addition of singlet and triplet bis(carbomethoxy)-carbene to the allyl halides and ethyl allyl sulfide. The

Table III. Competitive Reactions of Singlet and Triplet Bis(carbomethoxy)carbene to Allyl Compounds

Allyl compd	Singlet I	Triplet I
Allyl chloride	a, ^a 1 (standard) i, ^b 2.3	a, 1 (standard) i, 0.07
Allyl bromide	a, 1.0 i, 8.5 ^c	a, 1.0 i, 0.3
Ethyl allyl sulfide	a, 1.2 i, 6.3	a, 1.0 i, 0.5

^a a, addition product. ^b i, "insertion" product. ^c The product was unstable to prolonged irradiation.

data indicate that the singlet carbene attacks bromine and sulfur atoms about two times faster than it attacks a chlorine atom in an allylic position, as is expected from the electrophilic nature of the attacking carbene. On the other hand, the singlet carbene, as well as the

triplet carbene, adds to the double bond at almost equal rates irrespective of the nature of the allylic substrate.

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A Rhodium(II)-to-Rhodium(II) Single Bond in Bis(triphenylphosphine)tetrakis(dimethylglyoximate)-dirhodium

Sir:

In recent years it has been recognized that metal-to-metal bond formation occurs widely in transition metal compounds, and that the bonds vary considerably in strength.¹⁻³ Extremely short bonds of high multiplicity³ are in some ways the easiest to understand, whereas the longer, lower order bonds show considerable variations in length which are not always easy to explain. Just because these longer bonds are weaker, their lengths are very sensitive³ to factors such as the bulk and electronegativities of ligands, formal the oxidation state of the metal, and the geometric constraints imposed by bridging ligands when these are present.

Rhodium in its lower oxidation states apparently affords a variety of species containing Rh-Rh bonds. Several carbonyls (Rh₈(CO)₁₆, Rh-Rh 2.776 Å⁴) and cyclopentadienyl carbonyls ((*h*⁵-C₅H₅)₂Rh₂(CO)₃, Rh-Rh = 2.68 Å;⁵ (*h*⁵-C₅H₅)₃Rh₃(CO)₃, Rh-Rh = 2.62 Å⁶) have been studied structurally as has the Rh(II) compound Rh₂(O₂CCH₃)₄·2H₂O, for which only a rough structure with Rh-Rh ≈ 2.45 Å is reported.⁷ Recently several new dinuclear Rh(II) compounds have been prepared, e.g., Rh₂(DMG)₄(P(C₆H₅)₃)₂⁸ (DMG = monoanion of dimethylglyoxime) and Rh₂⁴⁺(aq).⁹ We have succeeded in obtaining a suitable crystalline form of the first of these and have determined its structure by X-ray diffraction in order to see what degree of metal-to-metal bonding might be present.

Crystals, grown from a solution in propanol containing a little H₂O, with the stoichiometry Rh₂(C₄H₇N₂O₂)₄[P(C₆H₅)₃]₂·H₂O·C₃H₇OH, belong to the monoclinic system; space group, P2₁/c; *a* = 18.695 (6), *b* = 13.417 (5), *c* = 22.817 (7) Å, β = 98.53°. The above formula represents the asymmetric unit of which there are four per unit cell. The structure was solved by direct methods and refined by full-matrix least squares, with the phenyl groups treated as rigid bodies. Approximately 3300 reflections whose intensities were $\geq 2\sigma$ (the esd based on counting statistics), collected within a sphere with $2\theta = 40^\circ$ (Mo K α), were employed. The Rh and P atoms were refined anisotropically. The final value

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