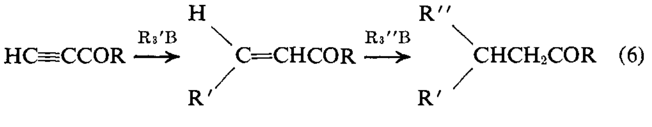
odically and analyzed by glpc. Analysis after 2 hr (60 ml of air or 0.5 mmol of O_2 was introduced) indicated that 6.5 mmol (a yield of 65%) of 4-cyclohexyl-3-butene-2-one had been formed. The ratio of the *cis*:*trans* isomer was 1.1:1.0.

The oxygen-induced reaction of organoboranes to acetylacetylene produces α,β-unsaturated ketones. These have previously been shown to undergo 1,4 addition with organoboranes. Consequently, the reaction appears capable of being controlled to introduce two different groups from two different organoboranes, making available a wide variety of ketones (eq 6).



$$HC\equiv CCOR \xrightarrow{R_3'B} \underset{R'}{\overset{H}{>}}C{=}CHCOR \xrightarrow{R_3''B} \underset{R'}{\overset{R''}{>}}CHCH_2COR \quad (6)$$

Perhaps even more significant is the fact that this development suggests the possibility of extending this oxygen-catalyzed addition of organoboranes to many other types of structures previously considered not to be applicable.

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[11] Postdoctorate research associate on Grant No. GM 10937 from the National Institutes of Health.

[12] National Institutes of Health Postdoctorate Fellow at Purdue University, Lafayette, Ind., 1969–1970.

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Insertion Reactions of ¹S Carbon Atoms in Double Bonds[1]

Sir:

Recent studies[2–5] have shown that carbon atoms attack olefins to give allenes, by a formal insertion of the carbon atom into the C=C double bond, and it has also been shown[6] that the reaction probably involves carbon atoms in the excited ¹S state (excitation energy, 2.7 eV[7]).

Recent studies[8] have shown that the MINDO/2 method[8a] can be used successfully to calculate potential surfaces[8a] for reactions involving hydrocarbons and also to study[8b] electron-deficient systems of the type involved in the intermediate phases of reactions of carbon atoms. We have accordingly calculated the relevant parts of the potential surfaces for the reaction of ¹S carbon atoms with ethylene and *trans*-2-butene and deduced the corresponding reaction paths. Preliminary trials showed that these involved approach of the carbon atoms in the plane bisecting the C=C bonds of the olefins, as one would expect; the perpendicular distance of the atom from the C=C bond axis was therefore taken as the reaction coordinate.

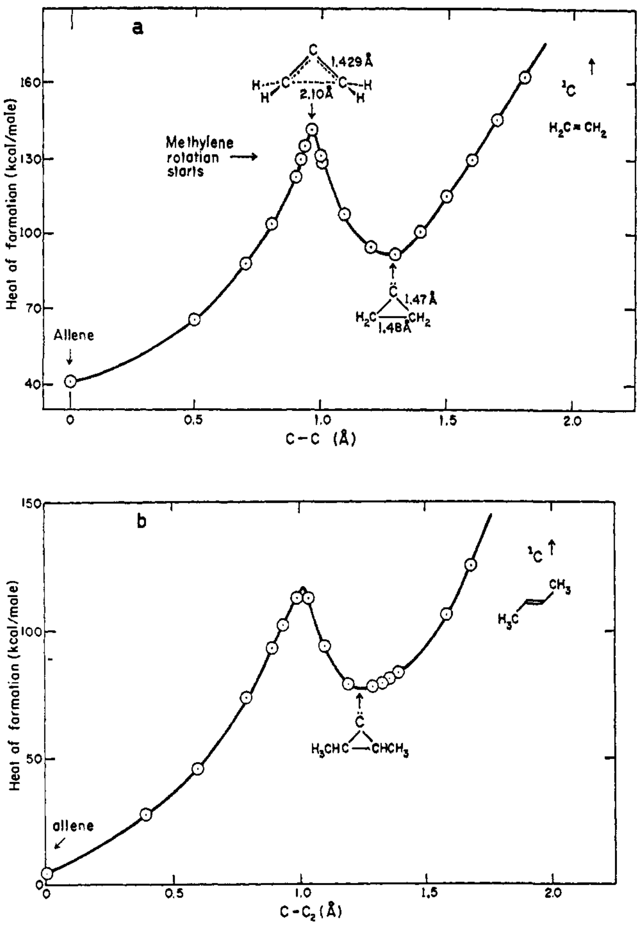
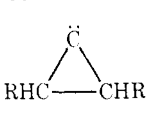


Figure 1. Reaction paths for reactions of carbon atoms with (a) ethylene, (b) *trans*-2-butene.

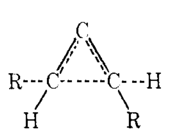
Figure 1a shows a section along the reaction path of the potential surface for the reaction of ethylene, and Figure 1b a corresponding plot for *trans*-2-butene. Each reaction falls into two distinct stages. In the first, a direct exothermic combination of the olefin with the carbon atom leads to a stable intermediate carbene I; in the second, I undergoes an activated rearrangement to the allene II.



Ia, R = H
b, R = CH_3

RHC=C=CHR

IIa, R = H
b, R = CH_3



IIIa, R = H
b, R = CH_3

The overall reaction involves a relative rotation of the methylene groups of ethylene, or the ethylidene group of *trans*-2-butene, since these are coplanar in the parent olefin but mutually orthogonal in the final allene, II. According to our calculations, this rotation takes place only in the final stages of the reaction, the original unrotated geometry being retained in the transition state, III, for conversion of I to II. The normal twisted form of II is the more stable only for CCC bond angles greater

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[1] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

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[5] J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

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[8] (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *ibid.*, in press; (c) M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **91**, 7521 (1969).

than those in III; ring opening in III therefore leads in effect to untwisted II. Rotation to form the normal twisted allene takes place only after the transition state is passed, *i.e.*, when the ring opening is effectively complete.

The calculated activation energies for the isomerizations of I to II are surprisingly large, 50 kcal/mol for Ia and 38 kcal/mol for Ib. These values seem unreasonable at first sight, given that allene is formed[6] by reaction of carbon atoms with ethylene in a neon matrix at −190°. However, on further reflection one realizes that the reaction paths of Figure 1 correspond to the particular normal mode of vibration which interrelates I and III; almost the whole of the energy liberated in the exothermic combination of the olefin with ^1S carbon to form I should therefore be converted into translational energy directly along the reaction path and the system should consequently pass straight over the transition state and on to I. Since the energy available (∼80 kcal/mol) is much greater than the activation energy for conversion of I to II, it is unlikely that the system will be quenched before crossing the transition state, since the time available is half that of a single molecular vibration. The only danger is that the system may not be quenched fast enough to trap II; this explains why addition of a moderator (neon) to the reaction mixture increases the yield of allene.[5,6] It is also easy to see on this basis why neither ^1D nor ^3P carbon atoms give allenes; in the case of ^1D carbon, the initial reaction is less exothermic, while in the case of ^3P the conversion of I to II would involve an intersystem crossing. Consequently in both cases products are formed[6] that are derived from I (spiropentane and cyclopropylidene derivatives). Indeed, the failure of ^1D carbon to form allene would be very difficult to explain if the activation energy for conversion of I to II were not large. It should be added that our estimates of the activation energies may well be too high by *ca.* 12 kcal/mol since the MINDO/2 method underestimates[8a] the strain energies of cyclopropanes by this amount.[9]

Allenes are also formed by reactions in solution where the carbenes, I, could have been intermediates, and this has been attributed to facile rearrangement of I to II.[11-15] Such processes, however, involve reactions of metals or metal alkyls with 1,1-dihalocyclopropanes and there is now abundant evidence that the intermediates in them are not free carbenes, but "carbenoids," in which the carbene is coordinated to the metal. Such a complex, $C_3H_4M^+$, is in effect a metallated cyclopropyl cation and could well rearrange more readily that I itself; we are at present calculating the potential surfaces for such reactions. It is interesting that the one reaction in solution that has been reported in which a free carbene would be expected to be an intermediate, *i.e.*, the reaction of N-nitroso-2,3-diphenylcyclopropylurethan with alkoxide in isobutene, led to a spiropentane formed by trapping of the intermediate diphenylcyclopropylcarbene[15] rather than to diphenylallene.

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[9] A referee has suggested that the transition state (III) might correspond to an orbital crossing and that configuration interaction might then reduce the calculated activation energy. This is not the case; the eigenvectors indicated no orbital crossing. It should be pointed out in this connection that our procedure has given[8a] good estimates of activation energies for rotation about CC bonds in ethylene and the cumulenes, processes in which orbital crossing does occur. Presumably this is because implicit allowance is made in the procedure for electron correlation by our use of parameters chosen to fit experimentally determined energies of atoms and molecules; inclusion of configuration interaction would then lead to an overestimate of the correlation energy. A similar situation arose in the treatment of radicals by a π approximation[10] in which the use of an open-shell SCF method gave heats of atomization that were too large.

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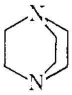
Long-Range Couplings between Lone Pair Electrons and Double Bonds[1]

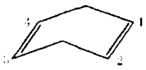
Sir:

Heilbronner and his collaborators[2] have recently shown by high-resolution photoelectron spectroscopy that there are strong interactions between the nitrogen lone pair AO's in dabco (I), and between the π MO's of 1,4-cyclohexadiene (II), norbornadiene (III), and bicyclo[2.2.2]octadiene (IV). The ionization potentials of nitrogen lone pair electrons, or olefinic π electrons, are less than those of electrons in σ bonds; I–IV each showed two distinct low-lying ionization potentials that must arise from mutual interaction of the lone pairs in I, or π MO's in II–IV.

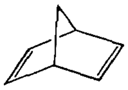
Hoffmann and his collaborators[3] had studied this problem in the case of I and concluded that there should be a large interaction between the nitrogen AO's and that this should arise not from a direct interaction across space but rather by a kind of hyperconjugative interaction *via* the intervening carbon atoms. Since the theoretical methods available to Hoffmann, *et al.*, were rather crude, and since we had become interested in this problem in the case of II–IV,[4] we have now examined it in detail, using a semiempirical SCF MO procedure (MINDO/2)[5] which has been shown to give good predictions of ground-state properties, including ionization potentials.[4,5] The contribu-

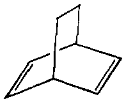


I



II


III


IV


V

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