Possible Symmetrical Addition of Singlet Methylene to Ethylene

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IT was recently demonstrated[1] that symmetrical addition of bent (C_{2v}) singlet methylene (CH_2) to ethylene in the fashion depicted in (I)† is disallowed by symmetry. On this basis, and apparently because the methylene involved in (I) is known to be the singlet of lowest energy, it was generalized that formation of cyclopropane from ethylene and singlet methylene cannot proceed in a symmetrical manner.‡ We presently demonstrate briefly that symmetrical addition of a more energetic linear ($D_{\infty h}$) singlet CH_2 to ethylene is both allowed by symmetry and, in some cases, plausible energetically.

The approach proposed here is shown in (II).† The level diagram correlating (II) with cyclopropane through a reflection operation is shown in the Figure.§ It is evident from this diagram that approach (II) is permitted by symmetry.

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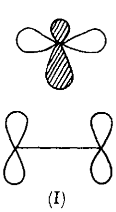
† In this, shaded areas represent fully occupied CH_2 orbitals, while clear sections denote totally vacant CH_2 orbitals.

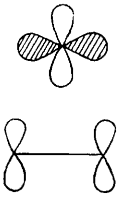
‡ The details of the unsymmetrical approach were examined by the "extended Hückel" method. On this basis, it was concluded that the energetically most favourable process should involve an initial "π" trimethylene-like approach, followed at shorter distances by the "σ" approach shown in (I).

§ "Walsh" cyclopropane M.O.'s are employed in the correlation diagram. For the number of levels shown, the same result may be obtained on the basis of the three centre "σ" M.O.'s employed previously (see ref. 1).

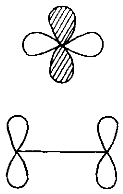
Interestingly, the alternative interaction by the same linear singlet, shown in (III),† is symmetry forbidden.



(I)



(II)



(III)

The energetic feasibility of the symmetrical addition (II) would clearly depend on: (a) the relative energies of the "symmetrical" and "unsymmetrical" transition states and (b) the availability of linear methylene under the reaction conditions.

Transition-state energetics certainly favour the symmetrical approach which involves concurrent generation of two bonds as opposed to the development of only one link in the unsymmetrical approach. Nevertheless, the energy difference between the two is not expected to be substantial in view of the high exothermicity of the reaction in question, which requires that the transition state resemble reactants rather than products. For example, employing $E_{C\text{-}C}$ (cyclopropane) = 70 kcal./mole[2] and $E_{C\text{-}C}$ (trimethylene) = 80 kcal./mole and assuming that bonding is only 10% complete in the transition state, we estimate an advantage of roughly 6 kcal./mole for the "symmetrical" transition state.¶

Fulfillment of the second requirement for a symmetrical approach, namely the availability of a linear singlet CH_2, depends primarily on the amount of energy imparted to the methylene upon fragmentation of its precursor. *Reacting* methylene is estimated[3] to carry excess energies of *ca.* 0, 5·5, 10·5, and 15·5 kcal./mole when photogenerated respectively from keten with 3130 Å, keten with 2800 Å, diazomethane with 4358 Å, and diazomethane with 3660 Å radiation. On the other hand, the most realistic calculations[4] place the lowest linear singlet** of methylene ($^1\Delta_g$) between 10 and 13 kcal./mole above the lowest bent singlet ($^1A_1$), while recent spectroscopic work[5] sets this energy difference at *ca.* 20 kcal./mole. These values are certainly quite close to the estimate of excess energy contained by reacting methylene when generated from diazomethane by way of the shorter wavelength radiation. On this basis, and bearing in mind the energetic advantage to be derived from the symmetrical approach, open only to linear $^1CH_2$, we conclude that: *reacting* singlet methylene, generated from diazomethane with 3660 Å radiation, may be linear†† and, this being so, that the addition of this species to ethylene ought to occur along the symmetrical pathway shown in (II). Furthermore, $^1\Delta_g$ methylene could conceivably be available for reaction in the other cases as well, if its excess energy added to the energy gained by following a symmetrical path equals or exceeds $E(^1\Delta_g) - E(^1A_1)$.

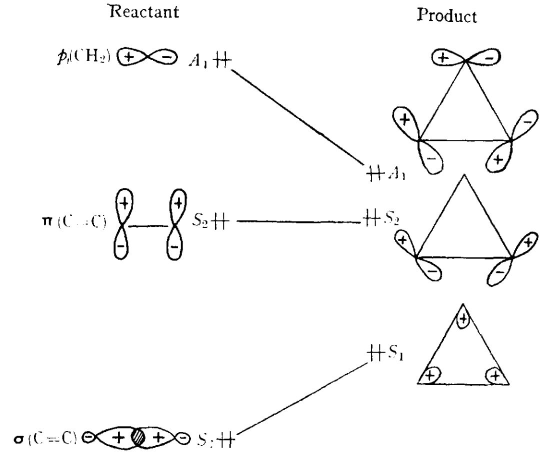


FIGURE. *Level correlation diagram pertaining to approach* (II).

Finally, we point out that in addition to being perhaps realizable under certain conditions, approach (II) is also intuitively more satisfying than either (I) or (III) as it (a) better depicts the known electrophilic character of singlet CH_2 and (b) requires no reorganization of its electronic distribution in generating cyclopropane (see Figure). A further attractive feature of approach (II) is that unlike (I) and (III) it disallows 1,4-addition of CH_2 to a diene, a process which has as yet to be

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¶ A similar value can also be obtained from the energy difference(s) between cyclopropane and trimethylene listed in reference 1.

** This linear singlet was chosen for its relatively low energy and because the configurational wavefunction of one of the two doubly degenerate $^1\Delta_g$ states satisfies the requirements of one fully occupied and one vacant p orbital imposed by the linear CH_2 shown in (II). $^1\Sigma_g{}^+$ methylene, believed to lie between 35[4] and 44[4] kcal./mole above the $^1A_1$ species also fulfills the requirement of the p orbitals.

†† $^1\Delta_g$ methylene may be viewed as highly vibrationally excited $^1A_1$ methylene.

realized experimentally. In fact, one can readily demonstrate that symmetrical interaction between singlet CH_2 and the end carbons of a conjugated polyene is symmetry-allowed through approach (II) for polyenes containing $4k + 2$ ($k = 0, 1, 2 \ldots$) π-electrons and through approaches (I) and (III) for polyenes containing $4k$ ($k = 1, 2 \ldots$) π-electrons.

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[5] G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. van Nostrand, New York, 1966, p. 583.