Regarding the Mechanism of Epoxidation of Olefins and Further Possible Applications of the 1,3-Dipolar Mechanism of Oxidations with Peroxy-acids

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ARGUMENTS have been presented[1] to contravene a suggested[2] 1,3-dipolar mechanism of olefin expoxidation with peracid. It was assumed[1] that norbornene and cyclohexene undergo all 1,3-dipolar addition reactions at the vastly different rates reported by Huisgen and his co-workers[3] for reaction with aromatic azides. The observed lack of rate difference of these olefins in reaction with peracid was then held to be evidence against any possible 1,3-dipolar characteristic of the epoxidation mechanism. But Huisgen has emphasized[4] that a 1,3-dipolar reagent without a double bond in the sextet structure should not necessarily show rate differences for reaction with these cyclic olefins. The hydroxycarbonyl oxide reagent assumed[2] to take part in the epoxidation mechanism is just such a structure.

However, a number of 1,2-dioxolans[5-7] have been described in the literature, which, if their structures are correct, appeared to be more stable than expected by the suggested epoxidation mechanism. Our n.m.r. and infrared analysis of purified 3-hydroxy-3,5,5-trimethyl-1,2-dioxacyclopentane (I) has confirmed the structural assignment of a 1,2-dioxolan suggested by Payne[7] on other grounds. Furthermore, it is evident that this compound, which according to the suggested[2] epoxidation mechanism would be formed directly from peracetic acid and isobutene in a 1,3-dipolar addition sequence, is considerably more stable than expected. We have studied weak acid catalysis of its decomposition and conclude that it is also quite stable to the acid conditions prevalent when isobutene is epoxidized in peracetic acid solution.

Warming a sample of (I) in deuterochloroform to temperatures below 100° caused spontaneous decomposition with formation of some isobutylene oxide. This establishes that the course of decomposition of the 1,3-dipolar adduct suggested to give rise to epoxide is possible. The other (major) products, however, indicate that other rearrangements can take place, attendant upon the scission of the O–O bond. The equations in Chart 1 summarize the product-forming reactions when the various conformations of (I) have been realized in which the two oxygens of the 1,2-dioxolan have achieved the (coplanar) repulsive interaction initiating bond rupture.

In each case the course of rearrangement may be correlated with the fulfillment of a geometric requirement for bond migration. The coplanity of four (*) centres in a transition state (VII) of concerted bond-making and -breaking can be recognized as the particular requirement for epoxide formation. The presence of substituents on the dioxolan ring, since they determine conformational energies and conformational interconversion barriers, largely control the proportions of products formed as (II), (III), or (IV).

It is thus apparent that the 1,2-dioxolan is never formed (as such) when the hydroxycarbonyl oxide reagent attacks olefin. One may recognize why this is so from consideration of the M.O. diagram (Figure) depicting the circumstances of approach to bond formation between superimposed interacting planes framing the cyclic (*via* hydrogen-bonding) carbonyl oxide 1,3-dipolar reagent and

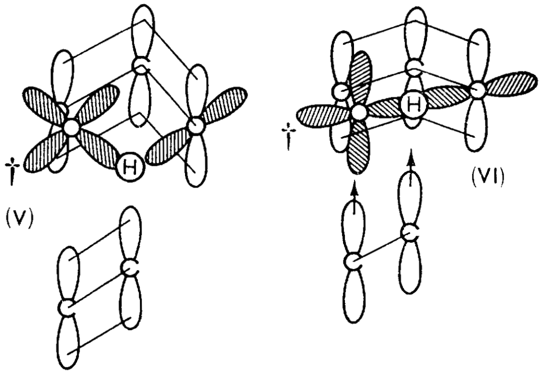

FIGURE. *Molecular-orbital representation of bond-forming steps.*

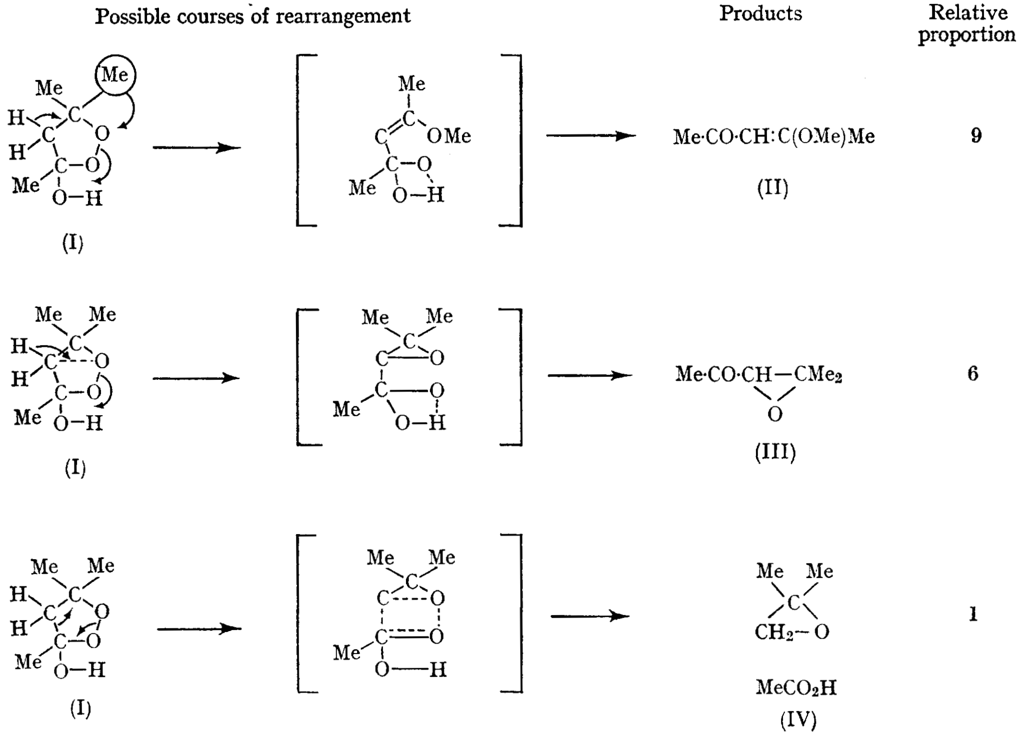

CHART 1. *Possible product-forming reactions on thermolysis of* (I) *at* 100—125° *in* 1:1 $CDCl_3$ *solution.*

the olefinic dipolarophile. The nonplanar (cyclic) reagent (V), in which the filled p-orbitals on the terminal oxygen (†) are staggered with respect to the π-orbitals on the other, represents a conformation of minimum repulsion along the O–O bond. Polarization in the transition state by the π-orbital of the dipolarophile [coming up to co-ordinate the terminal oxygen (†) and the carbon orbitals of the carbonyl oxide, as shown in (VI)] brings the filled p-orbital of this oxygen into a conformation in which it becomes eclipsed and highly repulsive with respect to its (σ) bonding-partner oxygen. At some point in the bond-forming process involving the terminal oxygen, when it is suffering a maximum amount of repulsive interaction with the adjacent oxygen, it lies sufficiently close to the second carbon of the dipolarophile to experience an attractive force. This event can best be perceived with the aid of Chart 2, the valence-bond representation of the transition state (VII). The very act of approach in (VII) to bond formation produces rearrangement to epoxide by virtue of the conformational accommodation that produces O–O bond rupture without intermediate formation of the 1,2-dioxolan (which would be the hypothetical non-planar, stable product of 1,3-dipolar addition).

This mechanism differs particularly from the earlier "butterfly" mechanism[8] in that it demonstrates the wide applicability of the 1,3-dipolar addition scheme, and the possibility of identifying its essential features[3,4] and kinetic manifestations in common reactions. Thus, it will be recognized that the product-forming characteristics[9a] and kinetics[9b] of the Baeyer–Villiger peroxy-acid oxidation of ketones are also in accord with a 1,3-dipolar mechanism of hydroxycarbonyl oxide addition to carbonyl, as illustrated in Chart 3.

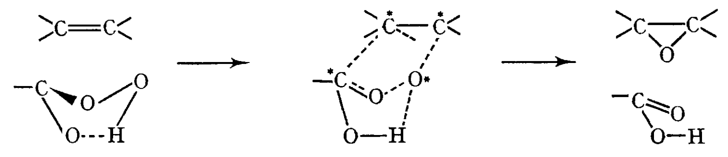
(VII)

CHART 2. *Valence-bond representation of the epoxide-forming transition state.*

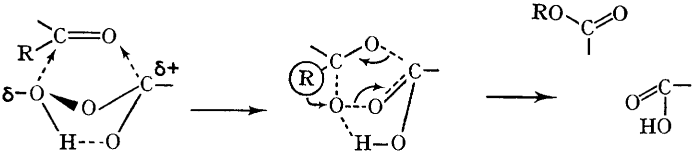

CHART 3. *An appropriate* 1,3-*dipolar path of the Baeyer–Villiger reaction.*

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