Tetrahedron Letters No.54, pp. 5677-5680, 1968. Pergamon Press. Printed in Great Britain.

DUALISTIC NATURE AND REPRESENTATION OF THE REACTIVE INTERMEDIATES ORIGINATING FROM n-π EXCITATION

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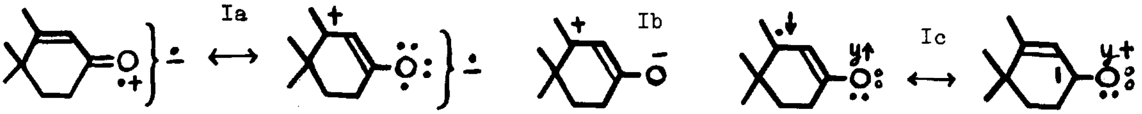
(Received in Japan 2 August 1968; received in UK for publication 1 October 1968)

Taylor (1) has recently criticized Chapman's polar state (2) as well as Zimmerman's electron demotion process (3), proposing a new representation of the photo-reactive intermediate originating from the n-π excitation. However it appears that none of these hypothetical formulation is satisfactory to explain the obviously antagonistic distribution of products. For example , Taylor's representation (Ia)(1), which on the subject of direction of charge distribution is nearly the same as Chapman's formulation (2), well accounts for the formation of hydroxy ketones of the type XIV (4,5) but does not appear to account for the formation of adducts of the type XVIII (x=OCH_3,CH_3)(6), or migration favoring the p-cyanophenyl over the phenyl group in 4-phenyl-4-(p-cyanophenyl)-cyclohexenone giving a product of the type XI (7). Zimmerman's representation (Ic)(3) which implies negative character on β-carbon seems to satisfy the later requirment. However the same treatment poses a question in explanation of the formation of the hydroxy ketone (XIV) unless an electron demotion process is specified.

These contradictions are resolved when we assume a dualistic nature of the intermediate species originating from the n-π excited state of the unsaturated carbonyl compounds; i.e. the β-carbon in VII, XIX, or XXI may be able to take both or positive and negative character. This may be visualized by referring to a simple molecular orbital model of α,β unsaturated ketone (II)(8). In the n-π transition, especially at an excited triplet state, there is a slight distortion of the conformation of anti- and non-bonding orbitals from the ground state condition (9,10). Thus shortly after the transition two ways in which electrons may interact arise.

Type A interaction is the interaction of an electron in an anti-bonding orbital with the π-bonding framework in II, where an electron is localized in a non-bonding

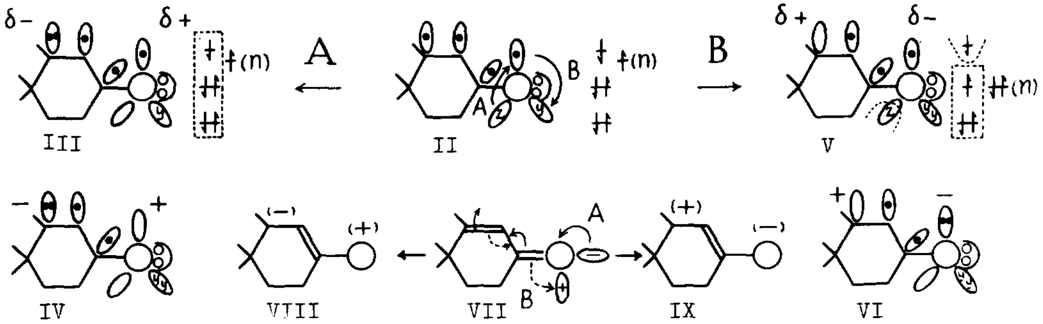


Ia

Ib

Ic

orbital. An extreme case of type A interaction is the π-system comprised of five electrons on four atoms, shown in III. M.O. calculation for this interacting system ($\psi_1^2\,\psi_2^2\,\psi_3^1$) indicated, for a crude test, that the β-carbon possesses negative charge density (-0.1233) compared to oxygen (+0.1371)(3,11).



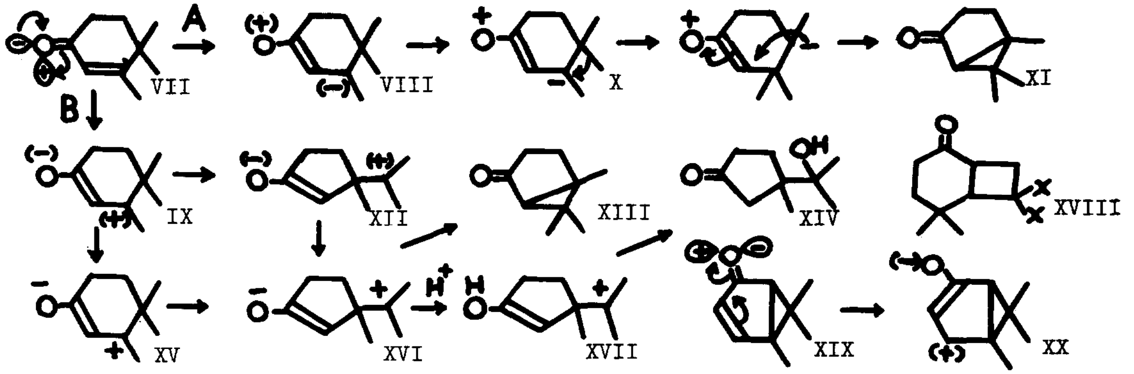
III II V

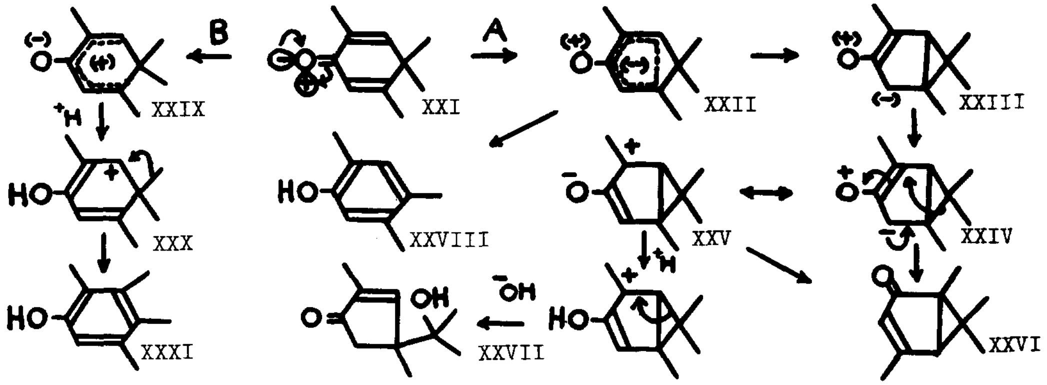
IV VIII VII IX VI

Type B interaction is the interaction of electrons in between the π-bonding framework and the non-bonding orbital in II, where an electron is localized in the anti-bonding orbital. When the anti-bonding electron in II is extremely localized in its orbital being out of the electronic interaction, a resulting π-system is of an electronic configuration $\psi_1^2\,\psi_2^2(\psi_n^1\,\psi_3^1)$. The electronic situation in this case is in close parallelism to that produced by electron impact of the α,β unsaturated ketone (12), and is analogous to that emphasized by Taylor (1). M.O. calculation (11) for this system ($\psi_1^2\psi_2^2(\psi_n^1\psi_3^1)$) indicated that the β-carbon takes positive character (+0.3445) compared to oxygen (-0.7768). The above species of the electronic configuration $\psi_1^2\psi_2^2(\psi_n^1\psi_3^1)$ may collapse to V when an energy level of the non-bonding orbital is lowered to have a sufficient interaction with the bonding orbital ψ_2(10,13). The type B interaction may occur when the electron in the non-bonding orbital is stabilized and accordingly the electron in the anti-bonding orbital is destabilized by such factors as solvation, substituent, geometrical effect etc., so that the type A interaction is prevented (14,15). These interaction type may be associated with the nature of the low-lying triplet state(15,16).

The excited zwitterions III and V, which have more radical like properties and are represented by conventional extreme formula VIII and IX respectively, give rise to reactive ground state molecules IV (or X) and VI (or XV) on the deactivation respectively. The type A and B interaction correspond formally to Zimmerman (Ic) and Taylor (Ia) or Chapman's (Ib) formulation for the reactive intermediate respectively (1,2,3). However it is important that the n-π excited state is able to generate both intermediates A (III or VIII) and B (V or IX). The choice of III or V as the reaction intermediate is based on the various environmental factors including solvent, substituent, migrating group, geometrical effect etc., and the reaction occurs predominantly via the energetically more favorable intermediate.

Therefore it is likely to represent the n-π excited state as VII, XIX, XXI, and formulate photochemical reaction paths as follows. A change of signs from (+) to + means that the deactivation of the excited to ground state molecule occurs at this stage (17). The formation of XIII from VII may occur via the type B interaction (IX) and a path way (IX → XII → XVI → XIII) may favor over that (IX → XV → XVI → XIII), because the formation of XIII has not been observed in the ground state reaction. Adduct (XVIII)(6) arises from the type A interaction. The type A interaction and subsequent zwitterions (XXIII - XXV) play a role for the formation of both lumiproduct (XXVI) and hydroxy ketone (XXVII) from the cross-conjugated ketone (XXI)(3,5,18). This is based on a fact that the calculated bond order (11) for the type A inter-





action (XXII) is positive (+0.0835) at the ββ' position while it is negative for the type B interaction ($\psi_1^2\psi_2^2\psi_3^2(\psi_n^1\psi_4^1)$)(XXIX) at the same position (-0.2618) (3). Phenol (XXVIII) also arises from the type A interaction (19). Contrary to those, phenol (XXXI) may arise from the type B interaction via cation (XXX)(5,20). Oppening of a cyclopropane ring in XIX occurs from the type B interaction, since the cyclopropane ring in XX interacts with the cation more potentially than the anion (21).

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