Molecular Orbital Consideration of the Reaction of the Zinc-Methylene Complex with Double Bonds

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It has been reported that a zinc-methylene complex prepared from methylene iodide and a zinc-copper couple reacts with olefins to give cyclopropanes, and with aldehydes to give olefins. The former reaction was suggested to be electrophilic, and the latter, nucleophilic. In this report this duality of the zinc-methylene complex and the reactivities of double bonds will be discussed in terms of the interaction between the reagent orbitals and the substrate orbitals. The reactivity of the carbonyl group will mainly be determined by the nucleophilic superdelocalizability of carbonyl carbon, while that of the olefinic double bond will mainly be determined by the electrophilic total delocalizability $(S^s_E + S^t_E + 2P^{st}_E)$. The theoretical predictions of these reactivities are consistent qualitatively with the experimental results.

It has been reported that methylene iodide and a zinc-copper couple gave an organozinc compound, which reacted with iodide to regenerate methylene iodide, which was hydrolyzed by water to methyl iodide, and which reacted with olefins to give cyclopropanes.[1] Recently we reported that the same organozinc compound reacted with aldehydes to give olefins in the presence of an excess of zinc.[2] Turnbull *et al.* have also reported that the above organozinc compound reacted with 3-keto-steroid having a 11β-hydroxyl group to give a 3-methylene steroid.[3] The solvent and substituent effects on

1) a) G. Emschwill, *Compt. Rend.*, **188**, 1555 (1929); b) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); c) *ibid.*, **86**, 1337, 1347 (1964).

2) S. Miyano, M. Hida and H. Hashimoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 174, 2134 (1966).
3) P. Turnbull, K. Syhora and J. H. Fried, *J. Am. Chem. Soc.*, **88**, 4764 (1966).

the reactions showed that the reagent attacked the double bonds of olefins as an electrophile, while the same reagent attacked the carbonyls of aldehydes as a nucleophile. This duality of reaction character is very interesting. The structure of the zinc-methylene complex[4] and the mechanisms of its reactions with double bonds have not yet been completely elucidated, but the above duality can be discussed in terms of the interaction between the zinc-methylene complex and double bonds. In this paper we wish to report that the above duality can be effectively understood in terms of the superdelocalizabilities of the double bonds.

Treatments by Reactivity Indexes

The stoichiometry of the reaction of methylene iodide and a zinc-copper couple and the chemical behavior of the resulting zinc-methylene complex indicated that 1 mol of methylene iodide had combined with 1 g atom of zinc to form the zinc-methylene complex; thus, the structure of the zinc-methylene complex was suggested to be $ICH_2\text{-}ZnI$, $(ICH_2)_2ZnZnI_2$, or their polymer form. It is supposed that the reactivity in the initial step of the reaction of the zinc-methylene complex with a double bond can be discussed in terms of the electron transfer between the pi-orbitals (π and $\pi*$) of the double bond and the orbitals (σ and $\sigma*$) of the reagent. The electron transfer from the occupied σ-orbital of the reagent to the unoccupied $\pi*$-orbitals of the substrate corresponds to a nucleophilic attack (Fig. 1(a)), while the electron transfer from the occupied π-orbitals of the substrate to the unoccupied $\sigma*$-orbital of the reagent corresponds to an electrophilic attack (Fig. 1(b)).
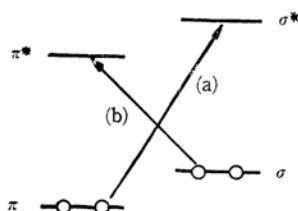

Fig. 1. The electron transfer between π- and σ-orbitals.

(a) electrophilic; (b) nucleophilic

Since the highest occupied and the lowest vacant levels contribute most importantly to these electron transfers, the frontier electron density shows that

TABLE 1. THE FRONTIER ELECTRON DENSITIES OF CARBONYL GROUP OF BENZALDEHYDE

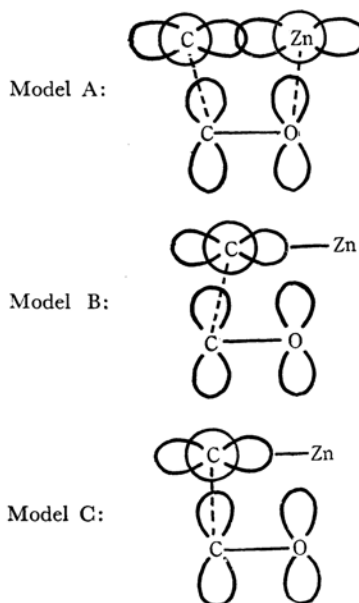| Atoms	Carbon	Oxygen
Electrophile	0.000	0.000
Nucleophile	0.8234	0.2976

Fig. 2. Three models of the interaction.

the reagent interacts with benzaldehyde as a nucleophile rather than as an electrophile (Table 1).

In this report three models of the interaction (one noncyclic model and two cyclic models) between the reagent and the double bond will be considered. By the second-order perturbation theory, the interaction energy (ΔE) can be represented by Eq. (1):

$$\Delta E = 2(\sum_j^{occ}\sum_k^{unocc} - \sum_j^{unocc}\sum_k^{occ})(H'_{jk})^2/(\varepsilon_j - \varepsilon_k) \quad (1)$$

where H'_{jk} is the interaction integral between the jth π-orbital (its energy, ε_j) and the kth reagent orbital (its energy, ε_k).

When these orbitals are expressed by linear combinations of the atomic orbitals, the interaction integral (H'_{jk}) is expressed by the atomic coefficients of the jth and kth molecular orbitals. In the A model H'_{jk} equals $(C_{sj}C_{s'k}+rC_{tj}C_{t'k})\gamma$, where s and t refer to atoms of the double bond, and s' and t', to methylene carbon and zinc respectively; where C's are their atomic coefficients; where γ is the resonance integral between the (s) and (s') carbons, and where r is the ratio of the resonance integral between the (t) and (t') atoms to γ. We have, therefore, Eq. (2):

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4) This organozinc compound is conventionally called zinc-methylene complex, since its structure has not yet been determined.

$$\Delta E = 2(\sum_{j}^{\text{occ}} \sum_{k}^{\text{unocc}} - \sum_{j}^{\text{unocc}} \sum_{k}^{\text{occ}}) \frac{(C_{sj}C_{s'k} + rC_{tj}C_{t'k})^2}{\varepsilon_j - \varepsilon_k} \gamma^2$$

$$= 2\left[\left\{ (C_{s'}^{\text{unocc}})^2 \sum_{j}^{\text{occ}} \frac{C_{sj}^2}{\varepsilon_j - \varepsilon_{\text{unocc}}} + r^2(C_{t'}^{\text{unocc}})^2 \sum_{j}^{\text{occ}} \frac{C_{tj}^2}{\varepsilon_j - \varepsilon_{\text{unocc}}} + r(C_{s'}^{\text{unocc}})(C_{t'}^{\text{unocc}}) \sum_{j}^{\text{occ}} \frac{2C_{sj}C_{tj}}{\varepsilon_j - \varepsilon_{\text{unocc}}} \right\} \right.$$

$$\left. - \left\{ (C_{s'}^{\text{occ}})^2 \sum_{j}^{\text{unocc}} \frac{C_{sj}^2}{\varepsilon_j - \varepsilon_{\text{occ}}} + r^2(C_{t'}^{\text{occ}})^2 \sum_{j}^{\text{unocc}} \frac{C_{tj}^2}{\varepsilon_j - \varepsilon_{\text{occ}}} + r(C_{s'}^{\text{occ}})(C_{t'}^{\text{occ}}) \sum_{j}^{\text{unocc}} \frac{2C_{sj}C_{tj}}{\varepsilon_j - \varepsilon_{\text{occ}}} \right\} \right]\gamma^2 \quad (2)$$

where only the sigma orbitals (ε_{occ} and $\varepsilon_{\text{unocc}}$) of C–Zn bond are considered to be reagent orbitals.

By using the expressions of $q^j{}_s$, etc. ($=2(C_{sj})^2$, etc.) and of $p^i{}_{st}$, etc. ($=2C_{sj}C_{tj}$, etc.), Eq. (2) can be rewritten as Eq. (3):

$$\Delta E = \frac{1}{2}\left[\left\{ q_{s'}^{\text{unocc}} \sum_{j}^{\text{occ}} \frac{q^j{}_s}{\varepsilon_j - \varepsilon_{\text{unocc}}} + 2rp_{s't'}^{\text{unocc}} \sum_{j}^{\text{occ}} \frac{p^j{}_{st}}{\varepsilon_j - \varepsilon_{\text{unocc}}} + r^2 q_{t'}^{\text{unocc}} \sum_{j}^{\text{occ}} \frac{q^j{}_t}{\varepsilon_j - \varepsilon_{\text{unocc}}} \right\} \right.$$

$$\left. - \left\{ q_{s'}^{\text{occ}} \sum_{j}^{\text{unocc}} \frac{q^j{}_s}{\varepsilon_j - \varepsilon_{\text{occ}}} + 2rp_{s't'}^{\text{occ}} \sum_{j}^{\text{unocc}} \frac{p^j{}_{st}}{\varepsilon_j - \varepsilon_{\text{occ}}} + r^2 q_{t'}^{\text{occ}} \sum_{j}^{\text{unocc}} \frac{q^j{}_t}{\varepsilon_j - \varepsilon_{\text{occ}}} \right\} \right]\gamma^2 \quad (3)$$

Since the molecular orbitals and energy levels of the reagent were not known, the reactive indexes were tentatively used. For example,

$$\sum_{j}^{\text{occ}} (q^j{}_s)/(\varepsilon_j - \varepsilon_{\text{unocc}})$$

can be replaced by an electrophilic superdelocalizability ($S^s{}_E$), and

$$\sum_{j}^{\text{unocc}} (-q^j{}_s)/(\varepsilon_j - \varepsilon_{\text{occ}})$$

by a nucleophilic superdelocalizability. Similarly,

$$\sum_{j}^{\text{occ}} (p^j{}_{st})/(\varepsilon_j - \varepsilon_{\text{unocc}})$$

and

$$\sum_{j}^{\text{unocc}} (p^j{}_{st})/(\varepsilon_j - \varepsilon_{\text{occ}})$$

can be replaced by an electrophilic bond-delocalizabilty ($P^{st}{}_E$) and a nucleophilic bond-delocalizability respectively.[5] The interaction index ($\Delta \varepsilon$ in $\frac{1}{2}\gamma^2$ unit) can be represented by Eq. (4):

$$\Delta \varepsilon = q_{s'}^{\text{unocc}} S^s{}_E + q_{s'}^{\text{occ}} S^s{}_N + 2r(p_{s't'}^{\text{unocc}} P^{st}{}_E - p_{s't'}^{\text{occ}} P^{st}{}_N) + r^2(q_{t'}^{\text{unocc}} S^t{}_E + q_{t'}^{\text{occ}} S^t{}_N) \quad (4)$$

In the B model, since H'_{jk} equals $(C_{s'k})(C_{sj}+rC_{tj})\gamma$, we have:

$$\Delta \varepsilon = q_{s'}^{\text{unocc}}(S^s{}_E + 2rP^{st}{}_E + r^2 S^t{}_E) + q_{s'}^{\text{occ}}(S^s{}_N - 2rP^{st}{}_N + r^2 S^t{}_N) \quad (5)$$

In the C model, H'_{jk} equals $(C_{s'k})(C_{sj})\gamma$; therefore, we have:

$$\Delta \varepsilon = q_{s'}^{\text{unocc}} S^s{}_E + q_{s'}^{\text{occ}} S^s{}_N \quad (6)$$

The Interaction between the Carbonyl Group and the Reagent. The ratio (r) of the resonance integral between oxygen and zinc (model A) or carbon (model B) to that between

carbons can be represented by overlap integrals. If we assume that methylene carbon and zinc have sp3-hybrid orbitals, and that the C–Zn bond is presented parallel to the C–O bond, the fourth term of Eq. (4) is negligibly small compared with the other terms, since $S_{\text{O–Zn}}$ may be so much smaller than $S_{\text{C–C}}$ that r is much smaller than 1. Table 2 reveals that $S^s{}_N$ is about ten times greater than $S^s{}_E$, and that $P^{st}{}_E$, $P^{st}{}_N$, and $S^t{}_N$ are linearly connected to $S^s{}_N$; therefore, Eq. (4) is transformed to Eq. (7):

$$\Delta \varepsilon = (q_{s'}^{\text{occ}} + a)S^s{}_N + b \quad (7)$$

where a and b are constants depending only on the molecular orbitals of the reagent, and perhaps are less determinative than $q_{s'}^{\text{occ}}$. In the B model (Eq. (5)), similarly, the interaction index ($\Delta \varepsilon$) is determined mainly by $S^s{}_N$ and r. It is noteworthy that the reactivity of the carbonyl group is connected with the superdelocalizability ($S^s{}_N$) of the carbon (s), and that the reactivity of the reagent is mainly connected with $q_{s'}^{\text{occ}}$. Since the more basic ether used as a solvent coordinates to zinc, and $q_{s'}^{\text{occ}}$ is made greater by the inductive effect, the activity of the reagent may be enhanced by the increased basic strength of the solvent. This is consistent with the experimental results.[2]

The reactivity of the carbonyl group is qualitatively determined by its superdelocalizability ($S^s{}_N$) in all three models, A, B, and C. From Table 2 the carbonyl compounds may be arranged in order:

p-chlorobenzaldehyde > benzaldehyde >

p-methylbenzaldehyde > *p*-methoxybenzaldehyde,

9-anthraldehyde > α-naphthaldehyde >

β-naphthaldehyde > benzaldehyde,

benzaldehyde > aliphatic aldehyde >

aliphatic ketone > methyl benzoate.

These theoretical results are consistent with the experimental results.[2,6]

5) K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, This Bulletin, **34**, 1076 (1961); The physical meaning was discussed by N. S. Ham *et al.* (*J. Chem. Phys.*, **29**, 1215, 1229 (1958)).

6) H. Hashimoto, M. Hida and S. Miyano, *J. Organometal Chem.*, in press.

TABLE 2. SUPER - AND BOND-DELOCALIZABILITIES OF CARBONYL GROUP

Compound		Electrophilic			Nucleophilic		
		S^s_E	S^t_E	P^{st}_E	S^s_N	S^t_N	P^{st}_N
p-X-Benzaldehydes:							
Cl	(I)	0.2317	0.6567	0.2044	2.8648	0.9728	1.6573
H	(II)	0.2365	0.6625	0.1989	2.7375	0.9126	1.5691
CH$_3$	(III)	0.2415	0.6667	0.1942	2.7119	0.9015	1.5529
OCH$_3$	(IV)	0.3492	0.7398	0.1047	2.3907	0.7602	1.3386
Naphthaldehydes:							
α	(V)	0.2961	0.7071	0.1460	2.7971	0.9571	1.6221
β	(VI)	0.2565	0.6761	0.1821	2.7575	0.9261	1.5861
9-Anthraldehyde	(VII)	0.4224	0.7945	0.0393	2.9233	1.0446	1.7288
Alkylaldehyde	(VIII)	0.1547	0.5774	0.2988	2.1548	0.5773	1.1153
Alkylketone	(IX)	0.1434	0.5996	0.2878	1.8100	0.4328	0.8687
Cinnamaldehyde	(X)	0.3349	0.7498	0.1871	2.8358	0.9999	1.6663
Acetophenone	(XI)	0.2254	0.6792	0.1938	2.3548	0.7436	1.3117
Benzophenone	(XII)	0.2665	0.7330	0.1367	2.7675	0.9830	1.6073
Benzoyl chloride	(XIII)	0.2495	0.6651	0.1873	3.1919	1.1359	1.8930
Methyl benzoate	(XIV)	0.4078	0.8681	0	1.3695	0.3488	0.6837

TABLE 3. SUPER - AND BOND-DELOCALIZABILITIES OF OLEFINIC DOUBLE BONDS

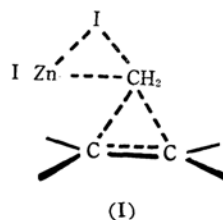| Compound		Electrophilic			Nucleophilic		
		S^s_E	S^t_E	P^{st}_N	S^s_N	S^t_N	P^{st}_N
β-Methylstyrenes:							
p-Methoxy	(I)	0.9765	1.7402	1.0983	0.8965	1.0920	0.9273
o-Methoxy	(II)	0.9730	1.7509	1.1020	0.8630	1.1027	0.9240
m-Methoxy	(III)	0.9837	1.2365	1.0216	0.9047	1.2365	0.9786
H	(IV)	0.9830	1.2390	1.0226	0.9039	1.2390	0.9774
Ethylenes:							
CH$_2$=CH$_2$	(V)	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
CH$_2$=CH→X	(VI)	0.7839	1.0261	0.4481	1.2149	0.9950	0.4481
CH$_2$=CH←X	(VII)	1.2149	0.9950	1.0996	0.7839	1.0261	1.0996
Styrene	(VIII)	0.9113	1.2662	1.0000	0.9113	1.2662	1.0000
1, 1-Diphenylethylene		0.8426	1.4994	1.0000	0.8426	1.4994	1.0000
Vinyl acetate (X)		0.9619	1.3402	1.1072	0.9619	0.8445	0.8928

Methyl benzoate may be expected to be unreactive, since it has a small S^s_N; it is indeed unreactive.[2] Although such other carbonyl compounds as aliphatic ketones, benzophenone, acetophenone, and benzoyl chloride (Table 2 (IX, XI, XII, XIII)) may be expected to possess considerable reactivities, those compounds did not give the corresponding olefins. It is likely that these results are to be ascribed to many causes, of which probably enolization and steric hindrance are most important.

The yield of phenylbutadiene from cinnamaldehyde was lower than that of styrene from benzaldehyde.[6] This fact was contrary to the prediction based on superdelocalizability (the values of the superdelocalizabilities of cinnamaldehyde and benzaldehyde are 2.8358 and 2.7375 respectively). This discrepancy may be ascribed to the side reaction, which gives 1, 2-bis(styryl)-ethylene glycol in a considerable amount.

The Interaction between Olefinic Double Bonds and the Reagent. Table 3 shows that the electrophilic delocalizabilities of the olefinic double bonds are larger than their nucleophilic delocalizabilities. This implies that the zinc-methylene complex behaves toward olefinic double bonds as an electrophile rather than as a nucleophile.

If we assume that the methylene transfer reaction passes through the transition state like I, and that the ratio, r, equals 1, the interaction index ($\Delta \varepsilon$) can be represented by Eq. (8):
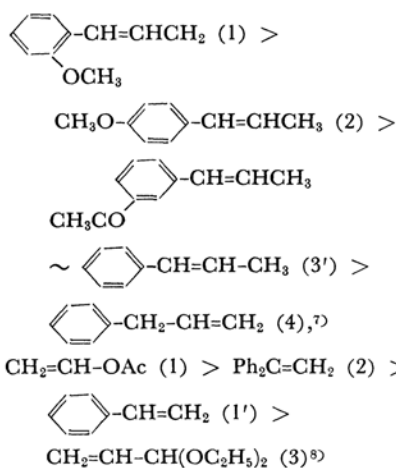
(I)

$$\Delta\varepsilon = q_{s'}^{\text{unocc}}(S^s{}_E + 2P^{st}{}_E + S^t{}_E)$$
$$+ q_{s'}^{\text{occ}}(S^s{}_N - 2P^{st}{}_N + S^t{}_N) \qquad (8)$$

If the reagent orbital in I posesses the character of a vacant p-orbital, the values of $q_{s'}^{\text{unocc}}$ and $q_{s'}^{\text{occ}}$ are approximately 1 and zero respectively. Table 4 further shows that the total electrophilic delocalizability, $(S^s{}_E + 2P^{st}{}_E + S^t{}_E)$, is more determinative than the total nucleophilic delocalizability, $(S^s{}_N - 2P^{st}{}_N + S^t{}_N)$. The total electrophilic delocalizability exhibits a decreasing order of the reactivities of olefins as follows:

TABLE 4.   TOTAL DELOCALIZABILITIES OF OLEFINIC
DOUBLE BONDS

Compound	Electrophilic	Nucleophilic
I	4.9133	0.1339
II	4.9279	0.1177
III	4.2634	0.1864
IV	4.2672	0.1881
V	4.0000	0.000
VI	2.7062	0.0011
VII	4.4028	0.9138
VIII	4.1775	0.1775
IX	4.3420	0.3420
X	4.5165	0.0208

$$\text{(benzene ring)}\text{-CH=CHCH}_2 \text{ (1)} >$$
$$\qquad \text{OCH}_3$$

$$\text{CH}_3\text{O-(benzene ring)-CH=CHCH}_3 \text{ (2)} >$$

$$\text{(benzene ring)-CH=CHCH}_3$$
$$\text{CH}_3\text{CO}$$

$$\sim \text{ (benzene ring)-CH=CH-CH}_3 \text{ (3')} >$$

$$\text{(cyclohexene ring)-CH}_2\text{-CH=CH}_2 \text{ (4),}^{7)}$$

$$\text{CH}_2\text{=CH-OAc (1)} > \text{Ph}_2\text{C=CH}_2 \text{ (2)} >$$

$$\text{(cyclohexene ring)-CH=CH}_2 \text{ (1')} >$$

$$\text{CH}_2\text{=CH-CH(OC}_2\text{H}_5)_2 \text{ (3)}^{8)}$$

These results are consistent with the experimental order shown in parentheses.[1b]

The vinyl part of cinnamaldehyde may be expected to be inactive toward an electrophile, since its total electrophilic delocalizability (1.000) is markedly low compared with that of other olefins. On the other hand, a considerable reactivity may be expected toward a nucleophile, since the total nucleophilic delocalizability (2.799) is not so low. The fact that no 1-phenyl-2-formylcyclopropane was formed shows that the methylene transfer reaction cannot have occurred through a nucleophilic mechanism.[9]

Parameterizations

In this report we used the parameters listed in Table 5. Several sets of different values of parameters of the carbonyl group have been used,[10] but the qualitative conclusions were not changed by the use of other sets of parameters of the carbonyl group. The computations of the Hückel molecular orbital and reactivity indexes were carried out on a HITAC 5020E computer (Tokyo University Computation Center).

TABLE 5.   THE PARAMETERS EMPLOYED

(1) Carbonyl groups
    Coulomb integrals: $\alpha_O = \alpha + 2.0\beta$
    For aromatic aldehydes and ketones:
                 $\alpha_C = \alpha + 0.2\beta$
    For aliphatic aldehydes: $\alpha_C = \alpha$
    For aliphatic ketones: $\alpha_C = \alpha - 0.2\beta$
    Resonance integrals: $\beta_{C=O} = 1.414\beta$

(2) Olefinic double bonds:
     $(t)\ (s)$
     $\text{CH}_2\text{=CH} \leftarrow \text{X} : \alpha_s = \alpha - 0.2\beta,\ \alpha_t = \alpha$
     $(t)\ (s)$
     $\text{CH}_2\text{=CH} \rightarrow \text{X} : \alpha_s = \alpha + 0.2\beta,\ \alpha_t = \alpha$

(3) Substituents:
    Cl; $\alpha_{Cl} = \alpha + 2.0\beta,\ \beta_{C-Cl} = 0.4\beta$
        $\alpha_{C\text{-ortho}} = \alpha + 0.2\beta,\ \alpha_{C\text{-meta}} = \alpha + 0.07\beta,$
        $\alpha_{C\text{-para}} = \alpha + 0.02\beta$
     $\text{CH}_3\text{O-}: \alpha_{CH_3O} = \alpha + 0.5\beta,\ \beta_{C\text{-OCH}_3} = 0.6\beta$
     $\text{H}_3\text{≡C-}: \alpha_C = \alpha - 0.1\beta,\ \alpha_H = \alpha - 0.5\beta,$
        $\beta_{C-H} = 2.5\beta,\ \beta_{C\ CH_3} = 0.7\beta$

(6) Other carbon atoms:
     $\alpha_C = \alpha,\ \beta_{CC} = \beta$

α: the Coulomb integral of a carbon sp² hybrid
β: the resonance integral for two bonding carbon sp² hybrids

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7) This compound is showed by $\text{CH}_2\text{=CH} \leftarrow \text{X}$ (inductive electron releasing effect) in Table 5.
8) This compound is showed by $\text{CH}_2\text{=CH} \rightarrow \text{X}$ (inductive electron drawing effect) in Table 5.

9)   But it was not yet known whether other nucleophilic reaction products were produced or not.
10)   C. A. Coulson, *Trans. Faraday Soc.,* **41**, 106 (1945); L. E. Orgel, T. L. Cottrel, W. Dick and L. E. Sutton, *ibid.,* **46**, 113 (1950); H. Baba and S. Suzuki, *J. Chem. Phys.,* **32**, 1706 (1960); G. Payette and C. Sandorfy, *ibid.,* **30**, 168 (1959).