CHEMISTRY LETTERS, pp. 389-392, 1983.

AN INTERPRETATION OF THE SUBSTITUENT EFFECT IN THE BLAISE REARRANGEMENT IN TERMS OF PI-ORBITALS

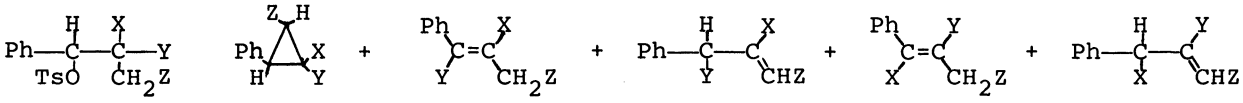
Yukio ABE and Tadashi SUEHIRO
Chemistry Department, Faculty of Sciences, Gakushuin University,
Mejiro, Toshimaku, Tokyo 171

The migratory aptitude of the substituent groups in the Blaise rearrangement can be explained in terms of the pi-electronic properties of the groups in the highest occupied molecular orbitals. The rates of the rearrangement reaction with relation to the substituent groups were also rationally understood based on the energy levels of the molecular orbitals.

The recent communication by Berner, Cox, and Dahn[1] on the mechanism of the Blaise rearrangement, indicating the role of the rearranged carbocation for the preferred migration of carboxylic group, prompted us to report our results of the studies on the rearrangement reaction.

In the Blaise rearrangement of compound 1a, the electron-withdrawing substituent group, ethoxycarbonyl, moves to the cationic carbon, which was formed by the cleavage of tosylate group, faster intramoleculary than the electron-releasing methyl group to yield 3.[2] This trend of the migratory aptitude was further confirmed by the examination of the reactions of 1c, 1d, and 1g. The compounds 1e and 1f showed apparently another trend of migratory aptitude of the groups. The product distributions of the rearrangement reactions are listed in Table 1.

Table 1. PRODUCT DISTRIBUTION OF THE BLAISE REARRANGEMENT (Yield in %)



	1			2	3	4	5	6
	X	Y	Z					
a[3]	CH_3	COOEt	H	5	58	0	0	4
b[3]	CH_3	COOEt	CH_3	5	30	21	0	0
c	CH_3	COPh	H	-	74	0	0	0
d	CH_3	CN	H	-	19	0	0	0
e	CH_3	Ph	H	-	85	0	0	0
f	CH_3	$CH=CH_2$	H	-	25	51	0	0
g	Ph	COOEt	H	-	27+19[4]	0	8[5]	33

The migratory aptitude of the substituent groups in 1a-g can be summarized as:

Ph, $CH=CH_2$, COPh, COOEt, CN $>$ CH_3, and Ph $\simeq$ COOEt.

The other nature of the substituent groups in the Blaise rearrangement was evident in the relative rates of the rearrangement of compounds 1a, 1c-f, and 1h (X=CH_3, Y=CH_3, Z=H). The rate of the rearrangement was measured from the initial slope of the decay curves of the starting materials at elevated temperatures: the reactions were accelerated by toluenesulfonic acid formed, exhibiting an auto-catalytic feature. The kinetic data are shown in Table 2.

Table 2. RATE AND ACTIVATION PARAMETERS OF THE BLAISE REARRANGEMENT

Compound	Y	$k(s^{-1})$	Temp. °C	Ea(kcal,mol^{-1})	$\Delta S^{\neq}$(e.u.)
1a	COOEt	$(3.6 \pm 0.4)\times10^{-5}$	160	22.3	-30
		$(1.5 \pm 0.2)\times10^{-5}$	145		
1c	COPh	$(4.5 \pm 1.0)\times10^{-5}$	130	16.5	-40
1d	CN	$(1.1 \pm 0.8)\times10^{-6}$	180	-	-
1e	Ph	$(4.5 \pm 0.8)\times10^{-5}$	115	21.6	-25
1f	$CH=CH_2$	$(2.8 \pm 0.3)\times10^{-5}$	115	23.0	-23
1h	CH_3	$(2.4 \pm 0.7)\times10^{-5}$	145	20.1	-33

The series of the rate enhancement caused by the substituent groups can be expressed as follows:

$$Ph > CH=CH_2 > COPh > COOEt > CH_3 > CN,$$

here the rate of the reaction 1h was devided by 3, in order to get the normalized rate. The entropy factor of the rearrangement reaction is characteristic, suggesting a transition state of multi-center interaction and/or of a rigid conformation such as shown in Fig. 1. The nature of the substituent effect in the intramolecular migratory aptitude together with that in the rates of the rearrangement can not be explained in terms of the usual measure of the substituent effect and we examined the substituent effect by means of the PMO theory.[6]

We took a simplified model of interaction between 1-phenylethyl cation and a substituted ethane $Y-CH_2-CH_3$ as shown in Fig. 2. The reaction partners are composed of benzylic cation derived from the ionic cleavage of the p-toluenesulfonate and the other molecular part of the starting compound in a de-methylated form, and the partners are assumed to lie paralell to each orther. This model is for the estimation of the stabilization energies due to the interactions between the cationic center and the ester group and between the cationic center and the methyl group. These interactions would occur in the starting molecules before they came into the transition state when the distances between the interacting centers were large as yet. Based on these stabilaization energies we tried to foresee the energy for the transition state of the ester migration relative to that of the methyl migration.[7]

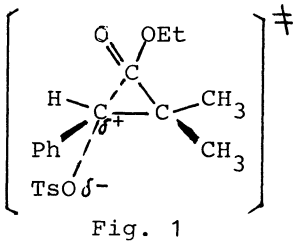


Fig. 1

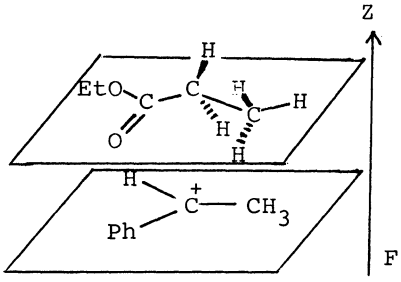


Fig. 2

The coefficient of the atomic orbitals of the relevant carbon of substituted ethanes in the pi-HOMO, and the energy levels of the orbitals were calculated by the standard INDO method (Table 3).

Table 3. COEFFICIENTS OF ATOMIC ORBITALS P_z OF SUBSTITUENT α-CARBON AND THE ENERGIES OF THE PI-HOMO OF Y–CH_2–CH_3

Y	Model compound for	Coefficient of P_z Y———CH_2———CH_3		Energy level eV	Energy difference[8]
COOEt	1a	0.2911	0.0020	-12.65	5.74
COPh	1c	0.2777	0.0065	-11.98	5.04
CN	1d	0.4166	0.1888	-15.15	8.21
Ph	1e	0.1285	0.0043	- 7.20	0.26
$CH=CH_2$	1f	0.5223	0.1110	-13.67	6.78
CH_3	1h	-	-	-15.47	8.53
	1g	MeOOC——CH_2———Ph			
	HOMO	0.0242	0.5278	-12.54	5.60
	2nd	0.2105	0.1090	-12.89	5.95
	3rd	0.1623	0.0460	-13.33	6.39

The relative amount of the stabilization energy due to the reaction between the benzylic cation (energy of LUMO: -6.94 eV) and the migrating group at the α-carbon can be estimated in a first approximation by means of the coefficient of the P_z atomic orbitals of the carbon atom: the migration of the substituent with large coefficient is preferred. The relative rate of the rearrangement of the compounds 1a, 1c-f, and 1h may be also deduced roughly from the energy difference between the LUMO of 1-phenylethyl cation and of the pi-HOMO of the substituted ethanes, the smaller energy difference leading to the larger reaction rate. The nearly equivalent migratory aptitude of Ph and COOEt groups can be explained by referring not only to the HOMO but also to the second and the third pi-HOMOs.

The migratory aptitude expected from Table 3 is just the same as that found in the experiments (Table 1). The relative rates of the rearrangement reaction deduced from Table 3 were as follows:

$$Ph \gg COPh \geqslant COOEt > CH=CH_2 > CN \geqslant CH_3 .$$

This series of relative rates of the rearrangement coinsides fairly well with the experimental results. Because we ignored the fine differences among the geometries of the transition states for compounds 1a, 1c-f, and 1h, some discrepancies between the experimental and estimated rate series are unavoidable. The vinyl compound would be expected to rearrange most rapidly, if we calculate the energy difference between vinyl cation and dimethylstyrene, assuming a model transition state which lies far more to the middle region of the reaction coordinate.[9] In our estimation we also neglected the effect of steric bulkiness of the substituent groups.[10]

We propose here an interpretation of the substituent effect in the Blaise rearrangement in terms of pi-molecular orbitals, assuming an early transition state in the reaction coordinate: the rearrangement of the substituent group can be promoted by the high pi-electron densities on the α-carbon of the substituent group which are indicated in the large coefficients of P_z atomic orbitals of the relevant carbons.

References

1) D. Berner, D. P. Cox, and H. Dahn, J. Am. Chem. Soc., 104, 2631 (1982).
2) E. E. Blaise and A. Courtot, Bull. soc. chim. France, 3, 35 (1906); T. Yokoyama and Y. Yukawa, Nippon Kagaku Zasshi, 82, 259 (1961).
3) Y. Abe and T. Suehiro, Chem. Lett., 1982, 337.
4) An intramolecular condensation product, 3-methyl-2-phenylindenone.
5) An intramolecular condensation product, 2-methyl-3-phenylindenone.
6) G. Klopman, J. Am. Chem. Soc., 90, 223 (1968); L. Salem, J. Am. Chem. Soc., 90, 543, 553 (1968); M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, N.Y. and London (1975). The stabilization energy due to the orbital interaction E may be expressed as follows:
$E = 2 \sum_{j}^{occ} \sum_{k}^{unoc} \frac{c_{rj}^2 \cdot c_{sk}^2 \cdot \beta_{rs}^2}{\alpha_j - \alpha_k}$, where c, β, and α denote coefficient of atomic orbital, resonance integral, and energy of the molecular orbital, respectively.
7) The treatment of the chemical reactivities by means of the PMO theory is cited for example in the article by R. F. Hudson, Angew. Chem., 85, 63 (1973).
8) Energy difference between pi-HOMO of substituted ethanes and the LUMO of 1-phenylethyl cation.
9) An attempted INDO calculation for the model reaction between alkyl cation and dimethylstyrene yielded a series of the relative rates of the rearrangement of 1a, 1c-f, and 1h as follows: $CH{=}CH_2 \gg COOEt > CH_3 \simeq Ph > COPh > CN$.
10) In the pinacol-pinacolone rearrangement of t-butyltrimethylethylene glycol, the migration of the t-butyl group is extraordinary rapid. This acceleration of the migration of the t-butyl group was deduced due to the steric bulkiness. M. Stiles and R. P. Mayer, J. Am. Chem. Soc., 81, 1497 (1957); V. J. Shiner and G. F. Meier, J. Org. Chem., 31, 137 (1966); P. D. Bartlett and T. T. Tidwell, J. Am. Chem. Soc., 90, 4421 (1968).

(Received January 6, 1983)