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An MO Interpretation of the Methylation of Olefins by the Methylsulfinyl Carbanion

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Recently the reaction of the methylsulfinyl carbanion with a number of olefins (quinoline, acridine, anthracene, butadiene, *etc.*) has been reported on by several authors. The superdelocalizability for the nucleophilic attack, $S_r^{(N)}$, is used as a theoretical index for discussing the intermolecular reactivity. It is pointed out that the calculated values of $S_r^{(N)}$ are useful in predicting the relative reactivity as well as the orientation in the nucleophilic aromatic methylation. In addition, the mechanism of the ring-opening reaction taking place with regard to benzofuran is discussed briefly.

Recently the reaction of the methylsulfinyl carbanion, $CH_3SOCH_2^-$, with a number of aromatic hydrocarbons and diolefins has been reported on by several authors.[1-5] Anthracene, quinoline, butadiene, and other conjugated molecules react with the methylsulfinyl carbanion in a dimethyl sulfoxide solution to form methylated derivatives, while 1,1-diphenylethylene and styrene are changed to 3,3-diphenylpropene and 3-phenylpropene re-

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[1] G. A. Russell, E. G. Janzen and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

[2] C. Walling and L. Bollyky, *J. Org. Chem.*, **29**, 2699 (1964).

[3] P. A. Argabright, J. E. Hofmann and A. Schriesheim, *ibid.*, **30**, 3233 (1965).

[4] G. A. Russell and S. A. Weiner, *ibid.*, **31** 248 (1966).

[5] H. Nozaki, Y. Yamamoto and R. Noyori, *Tetrahedron Letters*, **1966,** 1123.

spectively. However, benzene, naphthalene,[*1] pyridine, and phenazine do not react with the methylsulfinyl carbanion at all. Argabright *et al.*[3] and Nozaki *et al.*[5] considered that the nucleophilic attack of the methylsulfinyl carbanion on aromatic hydrocarbons is the rate-determining step. Russel *et al.*[4] and Nozaki *et al.*[5] showed that the products of quinoline, acridine, and other heterocyclic compounds can be predicted from the calculated charge densities. For anthracene and phenanthrene, however, the charge densities are found inadequate as a reactivity index.

In the present paper, we will use the superdelocalizability for the nucleophilic attack, $S_r^{(N)}$, proposed by Fukui *et al.*,[6] as a theoretical index for discussing the intermolecular reactivity, and will point out that the calculated values of $S_r^{(N)}$ are useful in predicting the relative reactivity as well as the orientation in the nucleophilic aromatic methylation. In addition, the mechanism of the ring-opening reaction of benzofuran is discussed briefly.

Method of Calculation

The superdelocalizability and the π-electron density were calculated from the Hückel molecular orbitals. The values of the parameters used are summarized as follows:

Coulomb integrals;

N: $\alpha+0.6\beta$, O: $\alpha+2\beta$

C (adjacent to nitrogen): $\alpha+0.1\beta$

C (adjacent to oxygen): $\alpha+0.2\beta$

Resonance integrals;

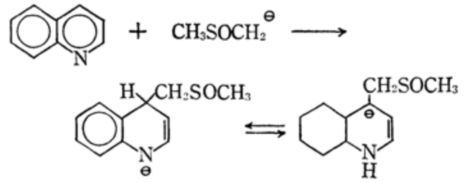
C–N: β, C–O: 0.6β

The parameters for a NO_2 group[7] and a CH_3 group[8] are the same as were given in Refs. 7 and 8.

The σ-electronic structure of benzofuran was calculated by the C–C skeleton method.[9,10]

Results and Discussion

Russell *et al.*[4] reported the mechanism of the methylation of quinoline to be as follows:



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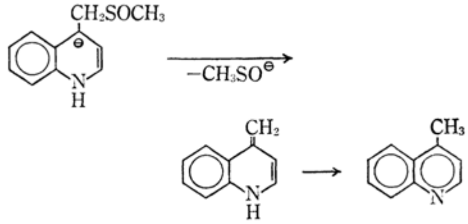

(2)

For 1,1-diphenylethylene, Walling *et al.*[2] reported the following mechanism:

$$CH_3SOCH_2^{\ominus} + CH_2{=}C(C_6H_5)_2 \rightleftharpoons CH_3SOCH_2CH_2C^{\ominus}(C_6H_5)_2 \tag{3}$$

$$CH_3SOCH_2CH_2C^{\ominus}(C_6H_5)_2 + CH_3SOCH_3 \rightleftharpoons CH_3SOCH_2CH_2CH(C_6H_5)_2 + CH_3SOCH_2^{\ominus} \tag{4}$$

$$CH_3SOCH_2CH_2CH(C_6H_5)_2 \longrightarrow CH_3SOH(?) + CH_2{=}CH{-}CH(C_6H_5)_2 \tag{5}$$

In Table 1, the calculated values of the superdelocalizability for a nucleophilic attack and the calculated values of the formal charge, Q_r, are listed and compared with the known experimental results.

As may be seen in Table 1, the calculated values of superdelocalizability agree fairly well with the experimental results as to the most reactive position in the molecules, and with the observed relative reactivity, for the nucleophilic aromatic methylation.

Namely, it is seen that all compounds except phenanthrene and phenazine[*2] can be classified into two groups by the magnitude of $S_r^{(N)}$: compounds with $S_r^{(N)}$ values larger than about 1.2 react with the methylsulfinyl carbanion to form methylated derivatives, whereas those with $S_r^{(N)}$ values smaller than about 1.2 are not methylated. Hence, this index may be used as a criterion to judge whether the compounds are methylated or not. Moreover, this agreement is considered to support the suggestion in Refs. 3 and 5, where the nucleophilic attack of the methylsulfinyl carbanion is considered

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[*1] A 15% yield of 1-methylnaphthalene has been recorded in 92 hr of heating (55°C).[3]

6) K. Fukui, C. Nagata, T. Yonezawa and K. Morokuma, This Bulletin, **34**, 230 (1959).

7) J. I. F. Alonso, *Compt. rend.*, **233**, 403 (1951).

8) Y. I'haya, This Bulletin, **28**, 376 (1955).

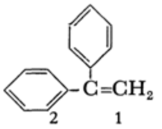
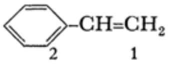
9) H. Yoshizumi, *Trans. Faraday Soc.*, **53**, 125 (1957); K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **33**, 1197 (1960).

10) K. Fukui, H. Kato, T. Yonezawa and S. Okamura, *ibid.*, **37**, 904 (1964).

[*2] For phenazine, the energy of the lowest vacant orbital (LV) is very low (α–0.153 β), and the partial π-electron density of nitrogen is the largest in LV. For this reason the calculated values of $S_r^{(N)}$ become much larger than in other compounds; also, that of nitrogen is the largest in the molecule.

If the coulomb integral of nitrogen is taken as $\alpha+\beta$, LV becomes non-bonding; consequently, the calculation of $S_r^{(N)}$ is impossible.

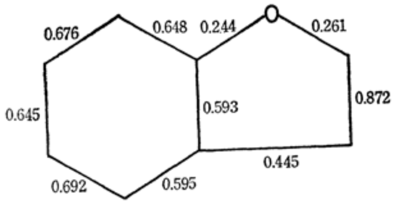
TABLE 1. THE SUPERDELOCALIZABILITY (S_r(N)) FOR THE NUCLEOPHILIC ATTACK AND THE FORMAL CHARGE OF THE π-ELECTRON (Q_r) IN COMPARISON WITH EXPERIMENTS

Compound (Experimental position of attack)	Position	$S_r^{(N)}$	Q_r	Reference
	1	1.499	0	2
(1)	2	0.925	0	
	1	1.266	0	2
(1)	2	0.931	0	
Butadiene	1	1.342	0	3
(1)	2	0.894	0	
Anthracene	9, 10	1.313	0	3, 4, 5
(9, 10)	1	1.073	0	
Phenanthrene	9	0.997	0	4, 5
(9)	1	0.977	0	
Quinoline	4	1.329	0.080	4, 5
(4)	2	1.224	0.083	
Isoquinoline	1	1.333	0.079	4, 5
(1)	8	1.076	0.016	
Phenanthridine	6	1.505	0.112	4
(6)	7	1.099	0.024	
Acridine	9	2.092	0.124	4
(9)	1	1.261	0.023	
1, 3-Pentadiene	1	1.324	−0.010	3
(1)	4	1.310	0.011	
Nitrobenzene	O	1.329	0.058	1
(O, P)	P	1.303	0.052	
Benzoxazole	2	1.860	0.080	4
(2)	3(N)	1.021	−0.195	
Benzene		0.833	0	3, 4, 5
(Unreactive)				
Naphthalene	1	0.994	0	3, 4, 5
(Unreactive)	2	0.873	0	
Pyridine	2	1.024	0.052	4, 5
(Unreactive)	4	1.017	0.059	
Phenazine	5(N)	3.153	−0.162	4
(Unreactive)	1	1.493	0.007	
Benzofurane	2	1.161	−0.070	4
(Ring-opening)	4	0.946	0.002	

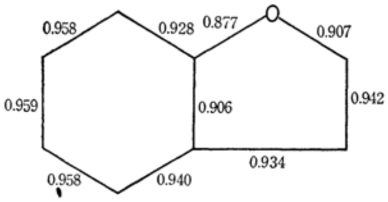
to be the rate-determining step in the methylation.

Russell *et al.*[4] compared the π-electron density with the methylated derivatives of quinoline, isoquinoline, phenanthridine and acridine, and pointed out that the most reactive position in the molecule has the largest positive formal charge. For benzene, naphthalene, butadiene, anthracene, styrene, and 1,1-diphenylethylene, however, all the formal charges are equally zero; hence, the formal charge, Q_r is not adequate as a reactivity index for discussing the orientation and relative reactivity.

In the methylation of benzofuran under normal conditions, it is known that this compound gives an essentially quantitative yield of *O*-hydroxy-phenylacetylene. That is, benzofuran exclusively undergoes the ring-opening reaction. Since the largest value of $S_r^{(N)}$ in benzofuran is 1.161, and so is smaller than 1.2, benzofuran is not methylated. On



The π bond order



The σ bond order

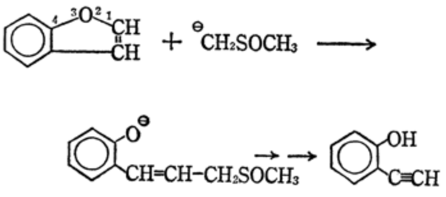
Fig. 1. The bond order of benzofuran.

TABLE 2. THE DELOCALIZABILITY ($D_r^{(N)}$) FOR THE NUCLEOPHILIC ATTACK OF BENZOFURAN

	Position*			
	1	2	3	4
$D_r^{(N)}$	2.702	1.675	1.793	2.636

* The numbering of benzofuran is shown in Eq. (6).

the ring-opening polymerization of β-propiolacton derivatives, Fukui *et al.*[10] reported that the reactivity index for the σ-electron system, that is, the delocalizability for a nucleophilic attack, ($D_r^{(N)}$), is useful in explaining the experimental result. This procedure is here extended to study the ring-opening reaction of the conjugated compounds. In the conjugated compounds, since each bond involves σ and π electrons, the bond strength may depend upon these populations. The calculated π-bond orders are shown in Fig. 1. The two C–O bonds are the weakest. For the elucidation of the σ-electronic structure of benzofuran, we made a calculation by the C–C skeleton method. The calculated σ-bond orders for the two C–O bonds are 0.907 and 0.877 respectively (Fig. 1); the calculated values of $D_r^{(N)}$ of the σ-orbitals are shown in Table 2. The position with the largest $D_r^{(N)}$ is the orbital 1. Consequently, it is considered that methylsulfinyl carbanion attacks the σ-orbital 1 of benzofuran nucleophilically and yields the intermediate (I).



(I)

(6)

The process from the intermediate (I) to the final products has been studied by extended Hückel method; the results will be published in the near future.