

g, 20 mmol) with activated zinc (1.3 g, 20 mmol) in 10 ml of acetic anhydride.<sup>13</sup>

In conclusion, trifluoromethyl group can be easily introduced into thebaine system *via* addition or Diels-Alder reaction which depends on the solvent, and plays an important role for the formation of retro Diels-Alder adduct.

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## Resonance Bond-Contraction Demonstrated by Cross-Interaction Constants

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The cross interaction constants  $\rho_{ij}$  in eq. (1) have been shown to be a very versatile tool for characterizing transition state (TS) structures, especially in  $S_N2$  reactions.<sup>1</sup> We present here a novel application of the cross-interaction constants to demonstration of resonance contraction of a bond in the  $S_N2$  TS.

$$\log(k_{12}/k_{21}) = \rho_{1i}\sigma_i + \rho_{1j}\sigma_j + \rho_{1i}\sigma_i\sigma_j \quad (1)$$

The sign of  $\rho_{ij}$  provides criteria for predicting substituent effects on the TS variation in  $S_N2$  reactions.<sup>1,c</sup> For example, if  $\rho_{XZ}$  is negative (Scheme 1), a stronger nucleophile ( $X = p\text{-OCH}_3$ ) as well as a stronger nucleofuge ( $Z = p\text{-NO}_2$ ) leads to a later TS so that eqs. (2) apply, whereas if  $\rho_{XZ}$  is positive the

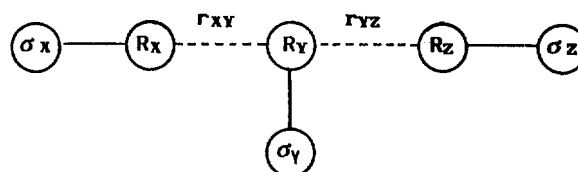
$$\left. \begin{aligned} \Delta r_{YZ} &= a\sigma_X & a < 0 \\ \Delta r_{XY} &= a'\sigma_Z & a' < 0 \end{aligned} \right\} \quad (2)$$

opposite effects are predicted so that the signs of  $a$  and  $a'$  in Eqs. (2) reverse to positive.<sup>1,c,2</sup> On the other hand, the distance  $r_{ij}$  in Scheme 1 is shown to be a logarithmic inverse function of the magnitude of  $\rho_{ij}$ <sup>2,3</sup> so that another set of relations are obtained with positive constants,  $b$  and  $b'$ , for

$$\left. \begin{aligned} \Delta \log |\rho_{YZ}| &= b\sigma_X & b > 0 \\ \Delta \log |\rho_{XY}| &= b'\sigma_Z & b' > 0 \end{aligned} \right\} \quad (3)$$

$\rho_{XZ} < 0$ , which reverse to negative ( $b, b' < 0$ ) for  $\rho_{XZ} > 0$ .

In our previous works, it has been shown that the  $S_N2$  reaction of anilines with benzyl benzenesulfonates, reaction (I)<sup>4</sup>, belongs to the former category *i.e.*,  $\rho_{XZ} < 0$  with negative  $a$  ( $a'$ ) and positive  $b$  ( $b'$ ), whereas that with phenacyl benzenesulfonates, reaction (II),<sup>1c</sup> belongs to the latter type, *i.e.*,  $\rho_{XZ} > 0$  with positive  $a$  ( $a'$ ) and negative  $b$  ( $b'$ ).

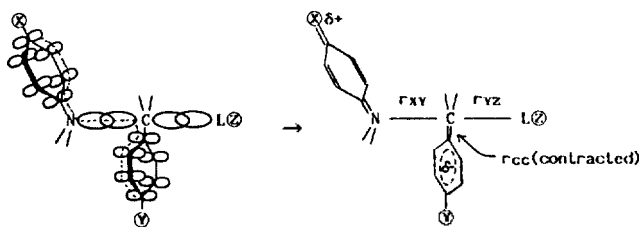


$i, j = X, Y$  or  $Z$  in eq. (1);  $r_{XZ} + r_{YZ}$ ,  $\sigma_i$  and  $R_i$  are substituents and reaction centers in the nucleophile (X), substrate (Y) and leaving group (Z).

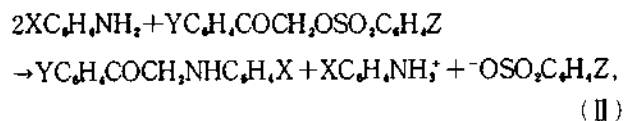
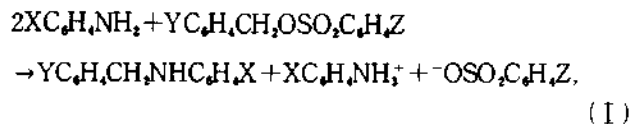
Scheme 1

**Table 1.** The  $\rho_{YZ}$  Values for Reaction I and II.

	$X = p\text{-OCH}_3$	$p\text{-CH}_3$	H	$p\text{-Cl}$	$m\text{-NO}_2$
Reaction I	0.35	0.20	0.11	0.13	0.14
Reaction II	-0.63	-0.65	-0.66	-0.67	-

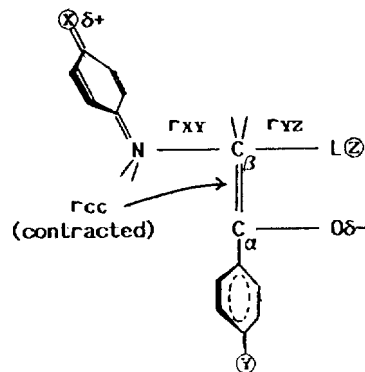


Two benzene rings are perpendicular to the paper plane.

**Scheme 2**

Thus  $r_{YZ}$  should decrease, and hence  $|\rho_{YZ}|$  should increase, as the nucleophile becomes weaker, *i.e.*,  $\Delta r_{YZ} < 0$  and  $\Delta \log |\rho_{YZ}| > 0$  for  $\sigma_X > 0$ , in reaction (I). The  $|\rho_{YZ}|$  value was indeed found to increase as the nucleophile gets weaker from  $X = \text{H}$  to  $X = m\text{-NO}_2$ , but  $|\rho_{YZ}|$  is seen to increase as the nucleophilicity increases from  $X = \text{H}$  to  $X = p\text{-OCH}_3$ , *i.e.*,  $\Delta \log |\rho_{YZ}| > 0$  for  $\sigma_X < 0$  and  $b > 0$ , in contradiction to the trend expected from eqs. (3) (Table 1). This inconsistency for the electron-donating substituents in the nucleophile ( $X = p\text{-CH}_3$  and  $p\text{-OCH}_3$ ) results from a "benzylic effect",<sup>5</sup> not from a decrease in  $r_{YZ}$  (Scheme 2). The substrate ring (with Y) attracts electrons from an electron-donating group, X, through  $\pi$ -overlaps involving the benzylic  $p$ -orbital, and as a result of this delocalization the bond between  $C_\alpha$  and the ipso-carbon atom of the substrate is contracted ( $\Delta r_{CC} < 0$ ). This means that the distance between substituents Y and Z can be reduced despite the increased bond cleavage due to a greater nucleophilicity ( $\Delta r_{YZ} > 0$  for  $\sigma < 0$  and  $a < 0$  in eqs. 2) so that  $|\rho_{YZ}|$  increases *i.e.*,  $\Delta r_{CC} < 0$  and  $\Delta r_{YZ} > 0$  but  $(\Delta r_{CC} + \Delta r_{YZ}) < 0$  since  $|\Delta r_{CC}| > |\Delta r_{YZ}|$  and hence  $\Delta |\rho_{YZ}| > 0$ . The delocalization of  $\pi$ -electrons on X is possible since the  $\pi$ -orbital in the aniline nucleophile can overlap with the benzylic  $p$ -orbital at an angle of ca.  $30^\circ$  which will provide more than 85% ( $\cos 30^\circ = 0.866$ )  $\pi$ -overlap.<sup>5a</sup> This benzylic effect is greater with a stronger nucleophile ( $\sigma_X < 0$ ), and hence  $r_{CC}$  in Scheme 2 becomes shorter ( $\Delta r_{CC} < 0$ ), since a stronger nucleophile leads to a tighter TS,<sup>6</sup> *i.e.*,  $\Delta r_{XY} < 0$ , and hence the overlap of the two  $\pi$ -clouds in the two rings becomes more efficient. In fact, use of the dual substituent parameter equations of the type in eq. (4) has shown a remarkably greater resonance-to-polar (reaction constant) ratio,

$$\log (k_Y/k_O) = \rho_{\text{pol}}\sigma_{\text{pol}} + \rho_R\sigma_R \quad (4)$$



Two rings are perpendicular to the paper plane.

**Scheme 3**

$\rho_R/\rho_{\text{pol}}$ , for such an electron-donating substituent ( $X = p\text{-CH}_3$  or  $p\text{-OCH}_3$ ) in the nucleophile<sup>7</sup> reflecting a strong resonance contribution to the substituent effects in the substrate ( $\rho_Y$ ).

On the other hand, we note in Table 1 that for reaction (II),  $|\rho_{YZ}|$  increases as the nucleophile becomes weaker ( $\sigma_X > 0$ ) suggesting a decrease in the distance between the substituents Y and Z. This appears to contradict with the trend expected from a reaction with  $\rho_{XZ} > 0$ , for which bond cleavage should increase and hence  $|\rho_{XZ}|$  should decrease with a weaker nucleophile since  $\Delta r_{YZ} > 0$  for  $a > 0$  and  $\sigma_X > 0$  in eqs. (2) for this type of reaction. This apparent inconsistency can be rationalized with the "resonance shunt" effect of the  $\alpha$ -carbonyl group.<sup>1c</sup> This effect is similar to the benzylic effect in that the overlap of  $\pi$ -orbital in the nucleophile and the  $p$ -orbital of the reaction center ( $C_\beta$ ) provides delocalization of electron density on the substituent X into the carbonyl oxygen in the TS resulting in a bond contraction,  $\Delta r_{CC} < 0$  (Scheme 3). Conjugation of X with the substrate ring is partially prevented by this "shunt" effect of the carbonyl group. However, the overlap of the reaction center ( $C_\beta$ )  $p$ -orbital and the  $\pi$ -orbital of the carbonyl carbon ( $C_\alpha$ ) is considerably more efficient, in addition to a strong electronegative electron-attracting effect of the carbonyl oxygen.

The resonance contraction of  $r_{CC}$  ( $\Delta r_{CC} < 0$  in Scheme 3) lead to an increase in  $|\rho_{YZ}|$ , which is not due to a decrease in  $r_{YZ}$ . In fact, bond cleavage should increase with a weaker nucleophile, *i.e.*,  $\Delta r_{YZ} > 0$  for  $\sigma_X > 0$  and  $a > 0$  for this type with  $\rho_{XZ} > 0$  in eqs. (2), so that an increase in  $|\rho_{YZ}|$  indicates a net decrease in the distance between Y and Z, *i.e.*,  $(\Delta r_{CC} + \Delta r_{YZ}) < 0$ , since  $|\Delta r_{CC}| > |\Delta r_{YZ}|$ . This work therefore demonstrates that the resonance contraction of  $r_{CC}$  is somewhat greater than the bond length changes involved in the TS due to substituent variation ( $\Delta r_{XY}$  or  $\Delta r_{YZ}$ ), so that  $\Delta r_{CC}$  ( $= r_{CC} - r_{CC} = 1.51 - 1.39 \approx 0.12 \text{ \AA}$ )<sup>13</sup> can cause an observable change in the magnitude of  $\rho_{YZ}$ , since  $\Delta r_{CC} < 0$  and  $\Delta r_{YZ} > 0$  but  $(\Delta r_{CC} + \Delta r_{YZ}) < 0$ ; this is reasonable since total bond length changes of 20~30%<sup>14</sup> ( $1.51 \times (0.2 \sim 0.3) = 0.30 \sim 0.45 \text{ \AA}$ ) in the TS are normally thought to occur, and hence  $\Delta r_{XY}$  or  $\Delta r_{YZ}$  due to substituent changes (10% of the total changes)<sup>15</sup> should be even smaller than this total bond length changes.

Furthermore the resonance contraction due to the "shunt" seems to be somewhat smaller compared to that due

to the benzylic effect, since the  $\Delta|\rho_{YZ}|$  values for changes in  $X$  from H to  $p\text{-OCH}_3$  were 0.03 and 0.24 for the former (reaction (II)) and for the latter (reaction (I)) respectively.

This type of resonance contraction ( $\Delta r_{CC} < 0$ ) can not be experimentally measured nor can be demonstrated with other selectivity parameters such as simple Hammett constants,  $\rho$ , or Brønsted constants,  $\beta$ ; the demonstration is only possible, at the present, with an observed increase in the magnitude of cross-interaction constants,  $\rho_{YZ}$ .

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### Reaction Mechanism for Acyl-Transfer Reactions of Aryl Acetates with Aryloxides

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Although acyl-transfer reactions have been known significantly important in chemistry and biochemistry and numerous studies have been performed, the reaction has not been well understood.<sup>1-3</sup> It has frequently been proposed that acyl-transfer reactions of aryl or thioaryl acetates with various amines and thiolates proceed *via* stepwise mechanisms, i.e. formation and breakdown of tetrahedral intermediates in which the rate-determining step may vary depending on nucleofugalities of the attacking and leaving groups.<sup>2</sup> However, until quite recently one step concerted mechanisms have also been suggested for most acyl-transfer reactions.<sup>3</sup>

The arguments concerning with the reaction mechanisms are mainly based on studies of linear free energy relationship (LFER), and the discrepancy seems to originate mostly from difficulties in interpretations of the effect of polar substituents in the attacking and leaving groups on rate constants. The LFERs including Brønsted and Hammett type treatment have been most commonly used for mechanistic investigations.<sup>4,5</sup> For many decades and for most reactions still today, the most valuable information on the determination of transition state (TS) structure has been obtained from the study of LFER.<sup>4-6</sup>

Recently we have reported that medium compositions would exert a significant influence on the  $\alpha$ -effect as well as on reaction rates for the acyl-transfer reactions of  $p$ -nitrophenyl acetate with oxygen centered nucleophiles.<sup>7</sup> Moreover, we have also observed unusual rate decreases upon addition of an aprotic solvent into the reaction medium. However, a plausible explanation for the results was not given