Theoretical Studies on the Gas-Phase Wolff Rearrangement of Ketocarbenes

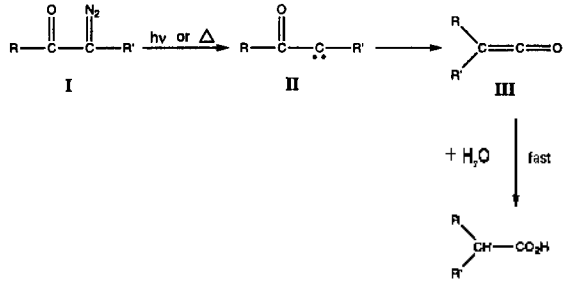
Chan Kyung Kim and Ikchoon Lee*

Department of Chemistry, Inha University, Inchon 402-751, Korea
Received January 21, 1997

The substituent effects in the gas-phase rearrangement of carbenes to ketenes involved in the Wolff reaction have been investigated theoretically using the AM1 method. In the initial state, carbene, there is a relatively strong vicinal n- σ* interaction between the lone pair (n) and carbonyl group (σ*). In the bridged transition state (TS), electronic charge is transferred from the migrating ring (Z-ring) toward the nonmigrating ring (Y-ring). The carbenes are stabilized by an electron donor Y ($\delta\sigma_Y<0$) whereas the TS is stabilized by an electron acceptor Y ($\delta\sigma_Y>0$). Multiple regression analysis of log (k_{YZ}/k_{HH})(= $-\delta\Delta G^{\ddagger}/2.3RT$) leads to a relatively large negative cross-interaction constant, $\rho_{YZ}=-0.53$, log (k_{YZ}/k_{HH})=2.96 $\sigma_Y^{-}-1.40\,\sigma_Z^{-}-0.53\,\sigma_Y^{-}\sigma_Z^{-}$ reflecting an extensive structural change in the transition state due to the stabilization of the initial state by the vicinal n- σ* overlap. When the solvent (water) effects are accounted for by the SM2. 1 model of the Cramer and Truhlar method, the magnitude of all the selectivity parameters, ρ_Y, ρ_Z and $\rho_{YZ}(=-0.66)$ are increased.

Introduction

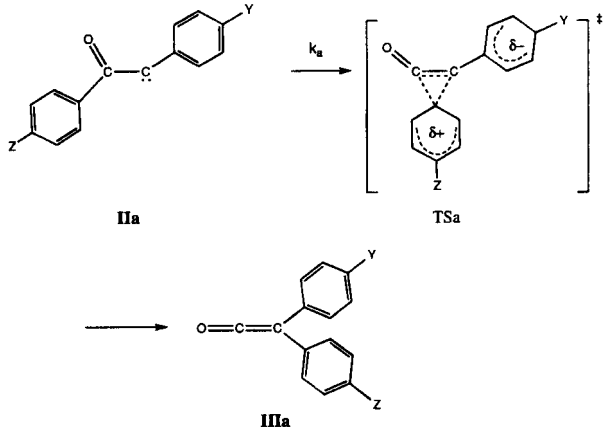
L. Wolff[1] isolated products formed by rearrangement of the carbon skeleton in decomposing dicarbonyl diazo compounds in aqueous solution, (1). The products were rationalized by assuming a ketene intermediate, III.



(1)

Azibenzil (R=R'=Ph in I) in MeOH at 50 °C afforded 70% of the Wolff rearrangement product, methyl diphenylacetate.[2] Elevated temperatures favor the Wolff rearrangement, and photolysis leads often successful "normal" rearrangement when other methods failed. Although the Wolff reaction may give a variety of final products, all of them can be derived from the intermediate ketene, III.[1] Thus, mechanistically the rearrangement process from singlet carbene, II, to ketene, III, is the most important step. In this work, effects of substituents in the two phenyl groups of azibenzil on the mechanism of the Wolff rearrangement in the gas phase, eq. 2, are examined.

For a disubstituted reaction system, we have been advocating nonadditivity of the substituent effects on the rate due to a cross-interaction term, ρ_{YZ}, in eq. 3.[3] This simple second-order expression is obtained by a Taylor series expansion of log k_{YZ} around $\sigma_Y=\sigma_Z=0$ with neglect of pure second-order (ρ_{YY} and ρ_{ZZ}) and higher-order (ρ_{YYZ} etc) terms. The cross-interaction constant, ρ_{YZ}, can be alter-



(2)

$$\log(k_{YZ}/k_{HH})=\rho_Y\sigma_Y+\rho_Z\sigma_Z+\rho_{YZ}\sigma_Y\sigma_Z \quad (3)$$

natively given by eq. 4, and is considered to represent a

$$\rho_{XY}=\frac{\partial\rho_Z}{\partial\sigma_Y}=\frac{\partial\rho_Y}{\partial\sigma_Z} \quad (4)$$

change in the intensity of interaction, ΔI_{YZ}, between the two substituents on going from the initial, I_{YZ}^{o}, to the transition state, $I_{YZ}^{\ddagger}$, eq. 5.[3b,6] The magnitude of ρ_{YZ} can therefore be

$$\rho_{YZ}\propto\Delta I_{YZ}=I_{YZ}^{\ddagger}-I_{YZ}^{o} \quad (5)$$

small when the two substituents interact strongly in the initial state as well as in the transition state (TS). The Wolff rearrangement is just such an example in which the migrating phenyl ring is initially (in carbene) bound by covalent bonds (strong interaction) but is partially cleaved in the TS with the two rings approaching nearer and interacting through dual routes (also strong interaction).

Calculations

The RHF/AM1 method[7] was used throughout in this

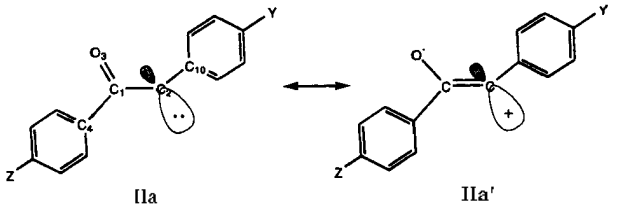
*To whom correspondence should be addressed.

work since the reactant, singlet carbenes, TS's and products have closed shell electron configurations. Geometries of all species were fully optimized and all stationary points were characterized by calculating the force-constant matrix and confirming all positive and only one negative eigenvalue for carbene and TS,[8] respectively. Entropies (S) were calculated to arrive at Gibbs free energies (G), at T=298 K, G=H-TS. The solvent (water) effects were accounted for by use of SM2.1 model of the Cramer and Truhlar method.[9] The free energy of solvation, ΔG_s, calculated by this method is the difference between the gas-phase and the aqueous-phase free energies. Since in this model the SCF results are parametrized using experimental data, they implicitly include electron correlation and configuration mixing effects[10] just as AM1 does for the gas-phase solute energies.

Results and Discussion

Structures

Carbenes (IIa). The structure of the singlet carbene, IIa, is shown in Figure 1. The lone pair orbital on C_2 overlaps with the σ antibonding orbital of the vicinal carbonyl



IIa IIa'

group, $\sigma^*_{C_1O_3}$ (n- σ* interaction).[11] This elongates the C=O) bond (1.25 Å *vs* 1.22 Å for the average of ketones[12]) but shortens the C_1-C_2 bond (1.42 Å *vs* 1.51 Å for the average value[12]). In addition, an electron donor *para*- substituent in the Y-ring, $\delta\sigma_y<0$ *(e.g.* Y=CH_3), intensifies this n- σ* interaction, and the distance between C_2 and C_{10}, $R_{2,10}$, becomes contracted as a result of conjugative electron donation from Y toward C_2 (1.388 Å with Y=CH_3 and 1.406 Å with Y=NO_2 for Z=H). As a result, the carbene, IIa, is stabilized *(vide infra)*. In fact the carbene is considered to form a resonance hybrid of IIa and IIa'. The bond distance

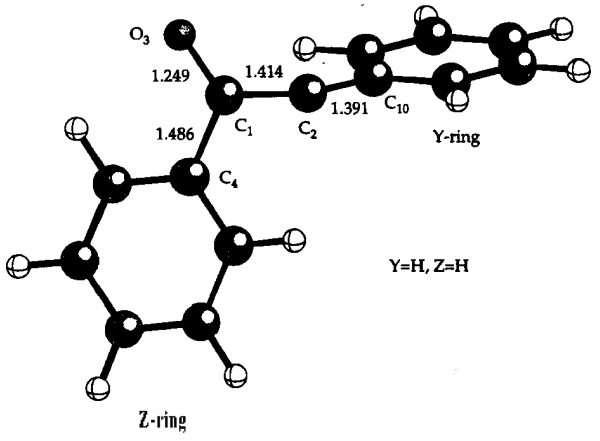
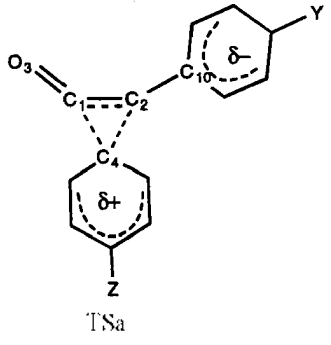


Figure 1. Structure of reactant (R). Y: H, Z: H. Bond lengths in Å.

data in Table 1 reveal that the two extremes of these structural effects are found with substitutent combinations of Y=CH_3; Z=NO_2(strongest effect) and Y=NO_2;Z=CH_3 (weakest effect); thus $R_{1,2}$ and $R_{2,10}$ are the shortest and the carbene is the more stable for the former, Y=CH_3;Z=NO_2 (ΔH_r=97.00 and 102.23 kcal mol^{-1}, respectively). In agreement with the resonance hybrid structure between IIa and IIa' due to the strongest n- σ* interaction between the lone pair and $\sigma^*_{C_1O_3}$ for the electron donor Y, $\delta\sigma_y<0$, the formal negative charge on O is larger (Table 2); q_o= − 0.345 and − 0.326, respectively, with Y=CH_3 and Y=NO_2 for Z=H. Charge distribution of the two rings in Table 2 reveals that in general the Z-ring is negative whereas the Y-ring is positive: the stronger the n- σ* interaction, the more negative is the Z-ring, the more positive is the Y-ring and the greater is the stability of the carbene *(vide infra)* due to the reso-



TSa

nance, IIa ↔ IIa'.

Transition states. The structure of the TS, TSa, is given in Figure 2. In the bridged TS structure, TSa, a partial double bond is formed between C_1 and C_2 with contraction of bond length of the bond C_1-C_2 and also C_1=O_3 (Table 1). These two bond contractions attending destruction of n- σ* interaction in the TS cause electronic charge flow from the Z-ring toward the Y-ring (Table 2). Thus the TSa becomes more stabilized by a stronger electron donor Z ($\delta\sigma_z<0$) and by a strong electron acceptor Y ($\delta\sigma_y>0$). In fact the relative order of stability becomes inverted on going from the carbene (IIa) to the TS; now bond length of the two bonds, C_1-C_2 and C_2-C_{10}, are the shortest and the TSa is the most stable for Y=NO_2; Z=CH_3.

Ketenes. The structure of the ketene is presented in Figure 3.

Energetics

Heats of formation (ΔH_f), entropies (S), activation and reaction parameters, $\Delta G^{\ddagger}$ and ΔG_r, are summarized in Table 3. In general, a stronger donor Z ($\delta\sigma_z<0$) and a stronger acceptor Y ($\delta\sigma_y>0$) destabilize the reactant, carbene (IIa), more ($\delta\Delta H_f > 0$), but stabilize the TS (TSa) more ($\delta\Delta H_f^{\ddagger}<0$) leading to a lower activation barrier, $\delta\Delta G^{\ddagger}<0$. This means that there is a relatively large structural change on going from the reactant, carbene IIa, to the TS.

In contrast, however, both stronger acceptors Z ($\delta\sigma_z>0$) and Y ($\delta\sigma_y>0$) stabilize the product, ketene, more leading to a greater exothermicity of the reaction, $\delta\Delta G_r<0$. Thus for a fixed Z, a stronger acceptor Y ($\delta\sigma_y>0$) leads to a greater exothermicity ($\delta\Delta G_r<0$) as well as a lower activation barrier

Table 1. AM1 optimized bond lengths of reactant, TS, and product in **Å**

Z	Y	Reactant					TS					Product				
		C_1-C_2	C_1-O_3	C_1-C_4	C_2-C_4	C_2-C_{10}	C_1-C_2	C_3-O_3	C_1-C_4	C_2-C_4	C_2-C_{10}	C_1-C_2	C_3-O_3	C_1-C_4	C_2-C_4	C_2-C_{10}
CH_3	CH_3	1.413	1.250	1.485	2.438	1.388	1.329	1.221	1.607	1.842	1.403	1.333	1.188	2.410	1.459	1.459
	H	1.414	1.249	1.485	2.438	1.392	1.329	1.221	1.605	1.845	1.403	1.333	1.188	2.410	1.459	1.459
	F	1.415	1.249	1.485	2.439	1.390	1.330	1.220	1.603	1.843	1.401	1.333	1.187	2.409	1.459	1.458
	Cl	1.416	1.249	1.484	2.439	1.393	1.329	1.221	1.598	1.849	1.400	1.333	1.187	2.409	1.460	1.457
	CN	1.420	1.248	1.483	2.440	1.399	1.323	1.221	1.583	1.861	1.388	1.334	1.186	2.407	1.461	1.455
	NO_2	1.425	1.247	1.482	2.442	1.406	1.327	1.220	1.576	1.860	1.384	1.335	1.185	2.406	1.463	1.452
H	CH_3	1.412	1.250	1.486	2.438	1.388	1.329	1.220	1.615	1.844	1.403	1.333	1.188	2.410	1.459	1.459
	H	1.414	1.249	1.486	2.438	1.391	1.329	1.220	1.613	1.847	1.403	1.333	1.188	2.410	1.459	1.459
	F	1.414	1.249	1.485	2.439	1.389	1.329	1.220	1.611	1.845	1.402	1.333	1.187	2.410	1.459	1.458
	Cl	1.415	1.249	1.485	2.439	1.392	1.329	1.220	1.607	1.850	1.401	1.333	1.187	2.410	1.460	1.458
	CN	1.413	1.248	1.484	2.440	1.399	1.321	1.220	1.591	1.863	1.389	1.334	1.186	2.408	1.461	1.455
	NO_2	1.424	1.247	1.483	2.442	1.406	1.325	1.219	1.584	1.861	1.385	1.335	1.185	2.406	1.463	1.452
F	CH_3	1.411	1.250	1.486	2.437	1.387	1.330	1.220	1.622	1.840	1.403	1.333	1.187	2.411	1.458	1.459
	H	1.413	1.249	1.486	2.438	1.390	1.330	1.220	1.610	1.844	1.404	1.333	1.187	2.411	1.458	1.459
	F	1.413	1.249	1.485	2.438	1.388	1.331	1.219	1.608	1.842	1.402	1.333	1.187	2.411	1.458	1.459
	Cl	1.414	1.249	1.485	2.439	1.391	1.331	1.220	1.604	1.847	1.402	1.333	1.187	2.410	1.459	1.458
	CN	1.418	1.248	1.484	2.440	1.397	1.323	1.220	1.587	1.862	1.390	1.334	1.186	2.409	1.460	1.456
	NO_2	1.423	1.247	1.483	2.441	1.404	1.326	1.219	1.580	1.860	1.385	1.335	1.185	2.407	1.462	1.452
Cl	CH_3	1.410	1.250	1.487	2.437	1.386	1.330	1.219	1.619	1.843	1.404	1.333	1.187	2.411	1.457	1.460
	H	1.412	1.249	1.487	2.437	1.390	1.330	1.219	1.617	1.846	1.404	1.333	1.187	2.411	1.458	1.460
	F	1.412	1.249	1.486	2.438	1.387	1.330	1.219	1.615	1.844	1.403	1.333	1.187	2.412	1.458	1.459
	Cl	1.414	1.249	1.486	2.438	1.390	1.330	1.219	1.611	1.849	1.403	1.334	1.187	2.411	1.458	1.459
	CN	1.418	1.248	1.485	2.439	1.397	1.322	1.220	1.594	1.864	1.390	1.334	1.186	2.409	1.460	1.456
	NO_2	1.422	1.247	1.484	2.441	1.404	1.325	1.219	1.585	1.862	1.385	1.335	1.185	2.407	1.462	1.453
CN	CH_3	1.408	1.249	1.489	2.435	1.384	1.329	1.218	1.636	1.849	1.405	1.334	1.186	2.413	1.455	1.461
	H	1.410	1.249	1.488	2.436	1.387	1.321	1.218	1.632	1.851	1.405	1.334	1.186	2.413	1.455	1.461
	F	1.410	1.249	1.488	2.437	1.385	1.329	1.218	1.631	1.849	1.404	1.334	1.186	2.413	1.456	1.460
	Cl	1.411	1.249	1.488	2.437	1.388	1.330	1.218	1.627	1.853	1.404	1.334	1.186	2.412	1.456	1.460
	CN	1.415	1.248	1.487	2.439	1.395	1.327	1.218	1.614	1.863	1.399	1.335	1.185	2.411	1.458	1.458
	NO_2	1.420	1.247	1.486	2.440	1.402	1.321	1.218	1.601	1.868	1.386	1.336	1.184	2.409	1.460	1.455
NO_2	CH_3	1.404	1.249	1.491	2.434	1.380	1.330	1.216	1.654	1.859	1.405	1.335	1.185	2.416	1.452	1.464
	H	1.406	1.249	1.491	2.435	1.384	1.330	1.216	1.652	1.861	1.406	1.335	1.185	2.415	1.452	1.463
	F	1.406	1.249	1.490	2.436	1.381	1.330	1.216	1.651	1.859	1.404	1.335	1.185	2.417	1.452	1.463
	Cl	1.407	1.248	1.490	2.436	1.385	1.330	1.216	1.648	1.862	1.405	1.335	1.185	2.415	1.452	1.462
	CN	1.412	1.247	1.490	2.438	1.392	1.330	1.216	1.637	1.868	1.404	1.336	1.184	2.413	1.454	1.460
	NO_2	1.416	1.246	1.488	2.440	1.399	1.317	1.216	1.621	1.879	1.389	1.337	1.183	2.411	1.456	1.457

($\delta\Delta G^{\ddagger}<0$), but for a fixed Y a stronger acceptor Z ($\delta\sigma_Z>0$) leads to a greater exothermicity ($\delta\Delta G<0$) but to a higher activation barrier ($\delta\Delta G^{\ddagger}>0$).

These energetic are in agreement with the results of substituent effects on the stabilities of the carbene, TS and ketene: the reactant is stabilized by the vicinal n_{C_2}-σ^*_{C-O} overlap whereas the TS is stabilized by the efficient electronic charge flow from the Z-ring toward the Y-ring. The ketene is obviously stabilized by lowering electronic charge from the ketene moiety, -C=C=O.

Cross-Interaction Constant ρ_{YZ}

The $\Delta G^{\ddagger}$ values in Table 3 are used to calculate the Hammett's ρ values by eq. 6. Since in the Y-ring relatively

$$\delta \log k_a = -\frac{1}{2.3RT}\cdot\delta\Delta G^{\ddagger} = \rho\cdot\sigma \qquad (6)$$

strong negative charge develops, the use[19] of σ^- rather than the normal σ improved the linear correlation substantially. We therefore used the σ^- constant for the substituent in the Y-ring, (σ_Y^-). The results are collected in Table 4. As predicted from the formal charges in Table 2, ρ_Z is negative and ρ_Y is positive indicating that electronic charge is lost from the Z-ring (positive charge develops) whereas it is gained in the Y-ring (negative charge develops) on going from the carbene to the TSs. Again the positive charge developed in the TS at C_4 is stabilized or partially neutralized by an electron donor Z (a less negative ρ_Z), while the negative charge developed in the TS on C_3 is stabilized by an electron acceptor Y (a less positive ρ_Y).

Multiple regression of $\Delta G^{\ddagger}$ (eq. 6) using eq. 3 gave the cross-interaction constant,[5] $\rho_{YZ}=-0.53$, as expressed by eq. 7. It is instructive to compare this expression, eq. 7, with

$$\log (k_{YZ}/k_{HH}) = 2.96\sigma_I - 1.40\,\sigma_Z - 0.53\,\sigma_I\,\sigma_Z \qquad (7)$$

the corresponding one for the base-catalyzed rearrangement

Table 2. Formal charges (q_i) of reactant (R) and changes in formal charges, $\Delta q'$ ($q'_i - q_i$), and Δq ($q_i - q_i$) in electronic charge unit

Z	Y	q_i						$\Delta q'$					Δq				
		C_1	C_2	O	Z-ring	Y-ring	C_4	C_1	C_2	O	Z-ring	Y-ring	C_1	C_2	O	Z-ring	Y-ring
CH	CH	0.268	-0.113	-0.350	-0.013	0.209	0.069	-0.080	0.056	0.045	-0.090	0.011	-0.094	0.215	0.045	-0.177	
	H	0.265	-0.105	-0.346	-0.010	0.196	0.074	-0.089	0.054	0.046	-0.085	0.014	-0.104	0.213	0.043	-0.166	
	F	0.267	-0.109	-0.345	-0.008	0.195	0.075	-0.092	0.055	0.049	-0.087	0.014	-0.100	0.215	0.045	-0.173	
	Cl	0.265	-0.102	-0.343	-0.007	0.187	0.082	-0.098	0.055	0.056	-0.094	0.018	-0.110	0.214	0.044	-0.167	
	CN	0.259	-0.084	-0.336	-0.001	0.162	0.118	-0.128	0.056	0.087	-0.134	0.031	-0.134	0.212	0.045	-0.155	
	NO_2	0.255	-0.061	-0.327	0.009	0.124	0.129	-0.155	0.060	0.095	-0.128	0.046	-0.165	0.212	0.046	-0.139	
H	CH	0.267	-0.114	-0.349	-0.015	0.211	0.068	-0.075	0.058	0.036	-0.087	0.012	-0.095	0.215	0.046	-0.179	
	H	0.265	-0.106	-0.345	-0.013	0.199	0.072	-0.084	0.056	0.037	-0.082	0.016	-0.105	0.213	0.044	-0.168	
	F	0.266	-0.110	-0.344	-0.010	0.198	0.073	-0.087	0.057	0.040	-0.084	0.015	-0.100	0.215	0.045	-0.175	
	Cl	0.264	-0.103	-0.342	-0.009	0.190	0.078	-0.091	0.057	0.045	-0.089	0.020	-0.110	0.214	0.045	-0.168	
	CN	0.259	-0.085	-0.334	-0.003	0.164	0.117	-0.123	0.059	0.078	-0.131	0.032	-0.134	0.212	0.046	-0.156	
	NO_2	0.254	-0.064	-0.326	0.006	0.130	0.129	-0.149	0.062	0.086	-0.127	0.047	-0.164	0.212	0.047	-0.143	
F	CH	0.270	-0.118	-0.348	-0.024	0.220	0.065	-0.069	0.060	0.035	-0.090	0.010	-0.091	0.218	0.046	-0.184	
	H	0.267	-0.109	-0.345	-0.021	0.207	0.069	-0.079	0.057	0.037	-0.084	0.014	-0.102	0.216	0.044	-0.172	
	F	0.269	-0.114	-0.343	-0.019	0.206	0.070	-0.081	0.059	0.039	-0.087	0.013	-0.097	0.218	0.045	-0.179	
	Cl	0.270	-0.106	-0.341	-0.017	0.198	0.074	-0.086	0.058	0.044	-0.090	0.018	-0.107	0.217	0.046	-0.173	
	CN	0.261	-0.088	-0.334	-0.012	0.172	0.112	-0.116	0.059	0.078	-0.132	0.030	-0.131	0.215	0.047	-0.160	
	NO_2	0.257	-0.068	-0.325	-0.003	0.139	0.127	-0.143	0.062	0.088	-0.133	0.045	-0.160	0.215	0.048	-0.149	
Cl	CH	0.268	-0.118	-0.347	-0.025	0.222	0.064	-0.065	0.061	0.029	-0.090	0.014	-0.093	0.218	0.045	-0.184	
	H	0.266	-0.109	-0.344	-0.022	0.208	0.069	-0.075	0.059	0.031	-0.084	0.018	-0.104	0.215	0.043	-0.172	
	F	0.268	-0.114	-0.342	-0.020	0.208	0.069	-0.077	0.060	0.033	-0.086	0.017	-0.099	0.218	0.044	-0.179	
	Cl	0.266	-0.106	-0.340	-0.019	0.200	0.073	-0.081	0.059	0.038	-0.089	0.021	-0.109	0.216	0.045	-0.173	
	CN	0.260	-0.088	-0.332	-0.013	0.173	0.113	-0.115	0.059	0.073	-0.130	0.033	-0.133	0.214	0.045	-0.160	
	NO_2	0.255	-0.069	-0.323	-0.004	0.140	0.128	-0.142	0.062	0.084	-0.132	0.047	-0.160	0.214	0.047	-0.148	
CN	CH	0.267	-0.123	-0.345	-0.034	0.234	0.061	-0.049	0.067	0.012	-0.091	0.022	-0.095	0.221	0.041	-0.189	
	H	0.265	-0.113	-0.341	-0.031	0.219	0.065	-0.061	0.064	0.015	-0.083	0.026	-0.107	0.218	0.039	-0.177	
	F	0.267	-0.119	-0.339	-0.029	0.220	0.066	-0.061	0.066	0.017	-0.088	0.024	-0.101	0.220	0.041	-0.185	
	Cl	0.265	-0.111	-0.337	-0.028	0.211	0.069	-0.067	0.064	0.020	-0.086	0.028	-0.111	0.219	0.041	-0.178	
	CN	0.259	-0.092	-0.329	-0.022	0.184	0.091	-0.091	0.062	0.040	-0.102	0.039	-0.135	0.216	0.043	-0.163	
	NO_2	0.254	-0.073	-0.320	-0.013	0.151	0.128	-0.132	0.065	0.069	-0.130	0.052	-0.160	0.215	0.044	-0.151	
NO_2	CH	0.268	-0.130	-0.342	-0.049	0.253	0.055	-0.024	0.076	-0.010	-0.097	0.033	-0.097	0.227	0.034	-0.197	
	H	0.265	-0.119	-0.337	-0.046	0.237	0.059	-0.036	0.072	-0.009	-0.087	0.036	-0.109	0.224	0.033	-0.184	
	F	0.268	-0.126	-0.336	-0.044	0.238	0.059	-0.035	0.074	-0.006	-0.092	0.035	-0.104	0.226	0.033	-0.191	
	Cl	0.265	-0.117	-0.334	-0.043	0.229	0.062	-0.042	0.072	-0.003	-0.089	0.038	-0.112	0.225	0.034	-0.184	
	CN	0.259	-0.098	-0.325	-0.037	0.201	0.075	-0.065	0.068	0.008	-0.085	0.047	-0.136	0.221	0.037	-0.169	
	NO_2	0.254	-0.078	-0.315	-0.028	0.167	0.125	-0.114	0.069	0.048	-0.128	0.058	-0.161	0.219	0.039	-0.154	

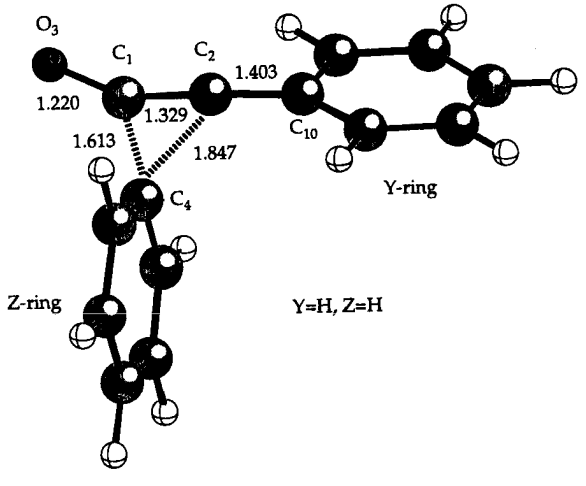


Figure 2. Structure of transition state (TS), Y H, Z H. Bond lengths in Å.

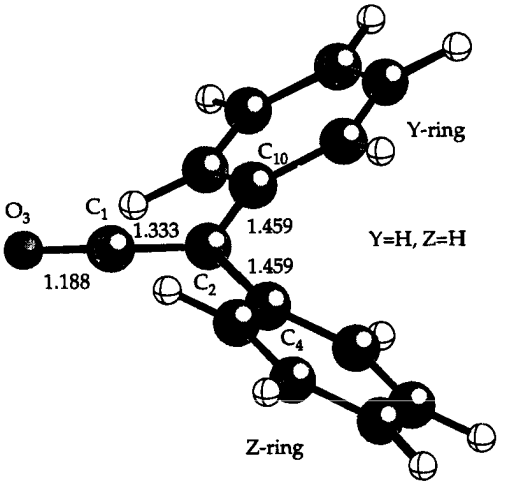


Figure 3. Structure of product (P), Y H, Z H. Bond lengths in Å.

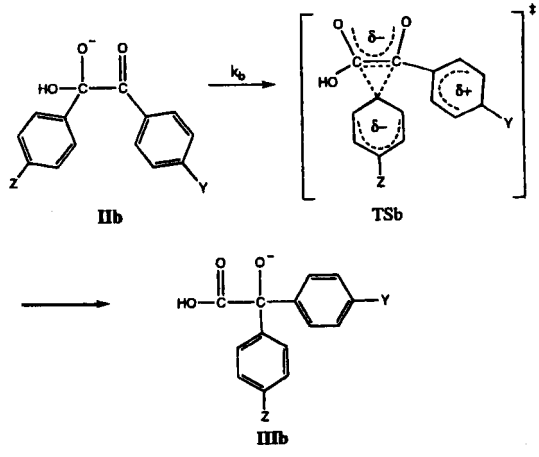
Table 3. Heats of formation, ΔH_f, entropies, S, Gibbs free energies of reaction, ΔG and of activation, $\Delta G^{\ddagger}$, in kcal mol^{-1}

Z	Y	ΔH_f			S			ΔG	$\Delta G^{\ddagger}$
		reactant	TS	product	reactant	TS	product		
CH_3	CH_3	85.49	107.30	30.88	133.39	132.18	131.89	-54.61	22.17
	H	93.89	115.15	38.56	124.54	123.07	121.69	-55.33	21.70
	F	48.48	69.86	-6.62	127.48	126.62	125.94	-55.11	21.64
	Cl	87.43	108.09	31.40	130.12	131.08	127.48	-56.03	20.37
	CN	127.96	146.15	69.86	132.37	131.93	129.15	-58.11	18.31
	NO_2	102.23	117.10	41.54	139.45	135.91	135.53	-60.70	15.92
H	CH_3	93.21	115.40	38.55	123.51	123.52	120.97	-54.66	22.19
	H	101.62	123.25	46.23	113.18	111.89	110.02	-55.39	22.01
	F	56.23	78.00	1.07	117.29	116.09	114.38	-55.16	22.12
	Cl	95.18	116.25	39.10	120.07	119.04	117.56	-56.08	21.38
	CN	135.74	154.51	77.58	122.12	122.11	119.34	-58.16	18.78
	NO_2	110.06	125.58	49.30	129.19	126.12	125.53	-60.76	16.44
F	CH_3	47.78	70.12	-6.62	127.57	127.89	124.88	-54.40	22.25
	H	56.24	78.01	1.07	117.25	115.99	114.80	-55.16	22.14
	F	10.91	32.83	-43.98	121.40	120.12	118.52	-54.88	22.31
	Cl	49.86	71.12	-5.96	124.25	123.03	121.84	-55.82	21.62
	CN	90.53	109.68	32.63	126.17	126.27	123.79	-57.89	19.12
	NO_2	64.99	80.87	4.51	133.03	130.41	129.80	-60.48	16.66
Cl	CH_3	86.06	108.72	31.40	130.11	128.91	127.79	-54.66	23.02
	H	94.52	116.62	39.10	120.02	118.64	117.01	-55.42	22.52
	F	49.18	71.45	-5.96	124.07	122.81	121.12	-55.14	22.64
	Cl	88.14	109.75	32.07	126.94	125.64	123.75	-56.07	21.99
	CN	128.81	148.37	70.68	128.93	129.10	126.20	-58.13	19.51
	NO_2	103.28	119.57	42.58	135.73	133.27	132.23	-60.70	17.02
CN	CH_3	124.89	148.42	69.86	131.90	130.51	128.47	-55.03	23.95
	H	133.40	156.39	77.58	121.76	120.47	118.92	-55.82	23.37
	F	88.13	111.31	32.63	125.89	124.57	122.94	-55.49	23.58
	Cl	127.09	149.66	70.67	128.68	127.37	125.71	-56.41	22.96
	CN	167.88	188.83	109.44	130.66	129.82	127.77	-58.44	21.19
	NO_2	142.52	160.33	81.56	137.24	135.42	133.36	-60.96	18.36
NO_2	CH_3	97.00	121.55	41.54	137.73	136.48	136.13	-55.46	24.93
	H	105.60	129.60	49.30	127.63	126.40	125.60	-56.30	24.37
	F	60.41	84.68	4.51	131.79	130.63	130.10	-55.90	24.62
	Cl	99.39	123.08	42.57	134.60	133.26	132.21	-56.81	24.09
	CN	140.36	162.69	81.56	136.56	135.26	133.40	-58.79	22.72
	NO_2	115.25	135.08	54.01	143.14	142.39	138.90	-61.24	20.06

Table 4. The Hammett's ρ_z and ρ_y values and cross-interaction constant, ρ_{zy}[a]

Z,Y	ρ_z	ρ_y
CH_3	-2.127 (0.968)	2.931 (0.974)
H	-1.883 (0.974)	3.045 (0.980)
F	-2.060 (0.978)	2.838 (0.966)
Cl	-2.442 (0.974)	2.930 (0.974)
CN	-3.165 (0.977)	2.574 (0.951)
NO_2	-2.845 (0.962)	2.184 (0.937)
	multiple regression	ρ_z = -1.399
		ρ_y = 2.955
		ρ_{zy} = -0.525 (0.941)

[a]correlation coefficient values are shown in parentheses.



(8)

of 4,4'-disubstituted benzils (IIb) in the gas phase, eq. 8.[11] For the benzilic rearrangement step, k_b, the multiple regression of the $\delta\Delta G^{\ddagger}$ data using eq. 3 gave the cross-interaction constant r_{yz} = − 0.48 as expressed in eq. 9.[11] In this

$$\log (k_{zy}/k_{xx}) = -1.76\,\sigma_z + 3.83\,\sigma_y - 0.48\,\sigma_z\sigma_y \qquad (9)$$

rearrangement, large electronic charge is carried by the *Z*-ring in the TS. The electronic charge in the TS partially comes from the C_2 moiety, and as a result the *Z*-ring is negatively charged and the C_2-moiety becomes positively charged in the TS. This is in quite contrast to those found in this work. For the benzilic rearrangement, eq. 8, the interaction between the two rings increases in the TS (relatively large magnitude of $\rho_{yz}(=-0.48)$), but in the rearrangement of the azibenzil (the magnitude of $\rho_{yz}(=-0.53)$) is slightly larger. Since the magnitude of ρ_{yz} represents the change in the intensity of interaction between the two substituents on going from the initial (IIa or IIb) to the TS (TSa or TSb),[5,6] eq. 5, the slightly greater magnitude of ρ_{yz} in the change from IIa to TSa as compared to that in the change from IIb to TSb may be ascribed to slightly greater increase of interaction: the relatively stable initial state in IIa due to the vicinal n- σ^* overlap could increase ΔI_{yz} and hence the magnitude of ρ_{yz} in eq. 5 for the azibenzil rearrangement. In both cases, *i.e.*, in TSa and TSb, the bridged TS structure causes considerable increase in the interaction between Y and *Z*.

Solvent Effects

Since the SM2.1 model of the Cramer and Truhlar method is a quantum statistical continuum-dielectric model, there is very little changes in the reactants, TSs and products structurally. In fact, we have shown that single point calculations on the energies and the Hammett coefficients pi and ρ_i using the gas-phase geometries (SM2.1/AM1//AM1) for the identity S_N2 reactions of (Y)-benzyl chlorides with Cl^- anion differ (<5%) very little from the corresponding values calculated by full optimization (SM2.1/AM1//SM2.1/AM1).[15] Thus, in this work, we carried out single point calculations.

The solvation energies, ΔG_{sol}, and the activation energies in water, $\Delta G^{\neq}+\Delta G_{sol}$, are summarized in Table 5. The activation energies in water obtained in this way are used to derive various selectivity parameters, ρ_Y, ρ_Z and ρ_{YZ}, by eqs. 6 and 3. The results are collected in Table 6. By comparison, all the ρ_Y and ρ_Z values have greater magnitude in aqueous solution. This is reasonable, since in this reaction charges are dispersed in the TS from the charge separated reactant, IIa', so that the solvent water stabilizes the reactant more than the transition state. In addition, there is a reversal of charge on going from the reactant (negative charge on the *Z*-ring and positive charge on the Y-ring) to the TS (positive charge on the Z-ring and negative charge on the Y-ring), Table 2, leading to a relatively large change in the solvation energy and hence to the greater magnitude of the p values. In accordance with this reversal of charge accompanied by a large structural change in water, the cross interaction between the substituents Y and Z, ρ_{YZ}, also increases with a larger magnitude of $\rho_{YZ}(=-0.66)$ in water. This is, however, in contrast with the solvent effects found for the benzilic rearrangement, in which negative charge (−1) is dispersed but without a reversal of charge in the TS. In the benzilic rearrangement, we found that the cross interaction between Y and Z decreased in water, to approximately by half.

We conclude that the Wolff rearrangements of α-ketocarbenes involve a charge-transferred bridged TS (TSa) from the migrating ring (*Z*-ring) toward the nonmigrating ring (Y-ring). However due to the relatively strong in-

Table 5. The solvation free energies (in kcal mol) and sum of the activation and solvation free energies (in kcal/mol) in aqueous solution

Z	Y	ΔG_{sol}	$\Delta G^{\neq}+\Delta G_{sol}$
CH_3	CH_3	2.39	24.56
	H	2.27	23.98
	F	1.78	23.41
	Cl	1.96	22.33
	CN	1.14	19.45
	NO_2	0.77	16.69
H	CH_3	2.44	24.63
	H	2.34	24.35
	F	1.85	23.97
	Cl	2.02	23.40
	CN	1.18	19.96
	NO_2	0.83	17.27
F	CH_3	2.53	24.77
	H	2.44	24.58
	F	1.96	24.27
	Cl	2.12	23.74
	CN	1.38	20.50
	NO_2	1.06	17.72
Cl	CH_3	2.57	25.59
	H	2.46	24.98
	F	2.01	24.64
	Cl	2.16	24.16
	CN	1.45	20.96
	NO_2	1.15	18.17
CN	CH_3	2.75	26.96
	H	2.66	26.03
	F	2.23	25.81
	Cl	2.35	25.32
	CN	1.88	23.07
	NO_2	1.55	19.90
NO_2	CH_3	2.72	27.65
	H	2.60	26.97
	F	2.17	26.79
	Cl	2.26	26.35
	CN	1.70	24.42
	NO	1.41	21.47

Table 6. The Hammett's ρ_Y and ρ_Z values and cross-interaction constant, ρ_{YZ} in aqueous solution

Z/Y	ρ_Y	ρ_Z
CH_3	-2.398 (0.979)	3.727 (0.984)
H	-2.162 (0.985)	3.840 (0.987)
F	-2.503 (0.983)	3.557 (0.979)
Cl	-2.704 (0.982)	3.619 (0.983)
CN	-3.697 (0.988)	3.133 (0.963)
NO	-3.407 (0.981)	2.804 (0.959)
	multiple regression	$\rho_Y=-1.566$
		$\rho_Z=-3.752$
		$\rho_{YZ}=-0.661$ (0.937)

[a]correlation coefficient values are shown in parentheses.

teraction caused by the vicinal n- σ* overlap in the initial state (IIa), the initial state is relatively stabilized. Moreover there occurs a complete reversal in the effects of substituents Y and Z from the initial to transition state, which will no doubt brings a relatively large structural change on going from the initial to the transition state. Thus there is relatively larger increase in the interaction between the two substituents, Y and Z, in the TS and hence results in a relatively larger magnitude of ρ_{yz}(= − 0.53) compared to that for the similar step in the base-catalyzed benzilic rearrangement (ρ_{yz}= − 0.48); for the latter no such initial state interaction exists and results in a relatively smaller increase in the interaction in the TS with a larger magnitude of ρ_{yz}. Charge dispersal in the TS leads to an increase in ρ_y, ρ_z and ρ_{yz} values in water.

Acknowledgment. We thank Inha University for support of this work. One of authors (C. K. Kim) also thanks the Korea Science and Engineering Foundation (961-0305-046-2) for support of this work.

References

1. Wolff, L. *Ann.* **1902,** *325,* 129.
2. (a) Wolff, L. *Ann.* **1912,** *394,* 23. (b) Staudinger, H.; Hirzel, H. *Ber. Deut. Chem. Ges.* **1916,** *49,* 2522. (c) Gilman, H.; Adams, Ch. E. *Rec. Trav. Chim.* **1929,** *48,* 464. (d) Georgian, V.; Boyer, S. K.; Edwards, B. *J. Org. Chem.* **1980,** *45,* 1686. (e) Tomioka, H.; Hayashi, N.; Asano, T.; Izawa, Y. *Bull. Chem. Soc. Japan,* **1983,** *56,* 758.
3. Schroeter, G. *Ber. Deut. Chem. Ges.* **1909,** *42,* 3356.
4. Kirmse, W. *Carbene Chemistry;* Academic Press: New York, U. S.A., 1964; p 118.
5. (a) Lee, I. *Chem. Soc. Rev.* **1990,** *19,* 317. (b) Lee, I. *Adv. Phys. Org. Chem.* **1992,** *27,* 57. (c) Lee, I. *Chem. Soc. Rev.* **1995,** *24,* 223.
6. Lee, I. *J. Phys. Org. Chem.* **1992,** *5,* 736.
7. (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. P.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985,** *107,* 3902. (b) MOPAC 6.0 program, available from Quantum Chemistry Program Exchange (QCPE) No. 506.
8. Csizmadia, I. G. *Theory and Practice of MO Calculations on Organic Molecules;* Elsevier: Amsterdam, 1976; p 239.
9. (a) Liotard, D. A.; Howkins, G. D.; Lynch, G. C.; Cramer, C. J.; Truhlar, D. G. *J. Comput. Chem.* **1995,** *16,* 422. (b) Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1991,** *113,* 8305. (c) Cramer, C. J.; Truhlar, D. G. *J. Comput. Chem.* **1992,** *13,* 1089, (d) Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1994,** *116,* 3892. (e) Giesen, D. J.; Storer, J. W.; Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1995,** *117,* 1057. (f) AMSOL 5.0 program, available, from Quantum Chemistry Program Exchange (QCPE) No. 606.
10. Storer, J. W.; Giesen, D. J.; Howkins, G. D.; Lynch, G. C.; Cramer, C. J.; Truhlar, D. G.; Liotard, D. A. *Structure and Reactivity in Aqueous Solution. Characterization of Chemical and Biological Systems;* Cramer, C. J., Truhlar, D. G. Ed.; American Chemical Society: Washington D.C., 1994; chapter 3.
11. (a) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1979,** *101,* 1700. (b) Weinhold, F.; Brunck, T. K. *J. Am. Chem. Soc.* **1976,** *98,* 3745. (c) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1976,** *98,* 4392. (d) Lee, I.; Cheun, Y. G.; Yang, K. *J. Comput. Chem.* **1982,** *3,* 565.
12. Sutton, L. E. Ed. *Tables of Interatomic Distances and Configurations in Molecules and Ions Special Publication No. 11,* The Chem. Soc.: London, 1958.
13. Exner, O. *Correlation Analysis in Chemistry;* Plenum Press: New York, 1978, chapter 10.
14. Lee, I.; Lee, D.; Lee, J. K.; Kim, C. K.; Lee, B.-S. *J. Chem. Soc. Perkin Trans 2,* **1996,** 2519.
15. Lee, I.; Kim, C. K.; Lee, B.-S.; Kim, C. K.; Lee, H. W.; Han, I. S. *J. Phys. Org. Chem.* submitted for publication, 1996.