4.83; N, 25.82. Found: C, 57.42; H, 4.59; N, 25.60.

**Analyses of Products from Decomposition of Arylazo-*tert*-alkylmalononitriles.** In cases of the solvents, methanol and $Me_2SO$, 0.3 mmol of **1a** was dissolved in 10 mL of a solvent and heated at 60 °C for 2 h. To the solution were added 10 mL of 5% $Na_2CO_3$ and 5 mL of $CCl_4$ containing a measured amount of 9,10-dihydroanthracene as an internal standard. The aqueous layer was extracted twice with 5 mL of $CCl_4$. The combined $CCl_4$ layers were washed with water, dried, carefully concentrated to 3 mL at atmospheric pressure, and subjected to NMR measurements. The aqueous layer was acidified with dilute HCl to yield **7b**, mp 223 °C dec, identical with the authentic sample [lit.[34] mp 215 °C]. With pyridine, the reaction mixture obtained under the same conditions was heated at 115 °C under nitrogen for 2 h prior to product analyses. With other solvents and substrates, the yields of products were determined by NMR measurements of the reaction mixture using a measured amount of an internal standard.

**Isolation of *N*-(*tert*-Cumyl)(*p*-nitrophenyl)hydrazonomalononitrile (14).** A solution of **1a** (1.25 g) in 5 mL of MeCN was heated at 60 °C for 3 h, and after 0.6 g of $NaHCO_3$ was added, the solvent was evaporated in vacuo. The residue was extracted with benzene and the extract, after it was treated with Norit, was concentrated to 10 mL, which gave a solid mass (0.44 g) upon addition of 10 mL of hexane. Recrystallization of the solid from benzene-hexane gave 0.34 g of **14** (27% yield) as pale-yellow needles: mp 137 °C dec; NMR $\delta$ 1.82 (s, 6 H), 6.94 (d, $J = 9.5$ Hz, 2 H), 7.2-7.5 (m, 5 H), 8.18 (d, $J = 9.5$ Hz, 2 H); IR ($cm^{-1}$) 2215 (s, CN), 2195 (m, CN). Anal. Calcd for $C_{18}H_{15}N_5O_2$: C, 64.85; H, 4.54; N, 21.01. Found: C, 64.93; H, 4.80; N, 21.00.

**Methylation of (*p*-Nitrophenyl)hydrazonomalononitrile (7b).** A mixture of 0.223 g of **7b** and 1 g of $Na_2CO_3$ in 10 mL of $Me_2SO$ was heated at 60 °C for 0.5 h and cooled at room temperature. To the reddish-orange mixture was added 3 mL of methyl iodide and, after the reaction mixture was stirred for 16 h, were added 1 mL of methyl iodide and 0.5 g of $Na_2CO_3$. After stirring for 8 h, the resulting mixture was treated with a mixture of 30 mL of benzene and 10 mL of 5% $Na_2CO_3$ and diluted with 50 mL of water. From the aqueous layer, 0.016 g (7%) of **7b** was recovered. The benzene layer gave 0.214 g (97% based on the unrecovered starting material) of the *N*-methylhydrazone **16** mp 140 °C (from ethanol); NMR $\delta$ 4.10 (s, 3 H), 7.53 (d, $J = 10$ Hz, 2 H), 8.30 (d, $J = 10$ Hz, 2 H); IR ($cm^{-1}$) 2220 (s, CN), 2210 (s, CN). Anal. Calcd for $C_{10}H_7N_5O_2$: C, 52.40; H, 3.08; N, 30.56. Found: C, 52.26; H, 3.06; N, 30.78. The absence of the C-methylated azo compound **17** was confirmed by direct comparison of NMR and IR spectra of the reaction mixture with those of the authentic sample. **17**: mp 85 °C [lit.[14] mp 87 °C]; NMR $\delta$ 2.21 (s, 3 H), 8.00 (d, $J = 8.00$ Hz, 2 H), 8.39 (d, $J = 8.34$ Hz, 2 H); IR ($cm^{-1}$) 2245 (vw, CN), 2200 (vw, CN). Anal. Calcd for $C_{10}H_7N_5O_2$: C, 52.40; H, 3.08; N, 30.56. Found: C, 52.29; H, 3.11; N, 30.60.

**Kinetic Experiments.** The rates of decomposition were determined by monitoring the disappearance of the methyl peak of a substrate relative to a peak of an internal standard in the NMR spectrum as a function of time. Anisole was used as the internal standard except for the following cases: *p*-xylene for **1g** and hexamethylethane for **21** (hexamethyldisiloxane for **21** in methanol-$d_4$). Commercially available deuterated solvents dried with molecular sieves (3- or 4-Å) and purified pyridine were used in the kinetic measurements. Initial concentrations were ca. 0.08 M. The sealed NMR tube was heated directly in the NMR probe or in a thermostated water bath (±0.01 °C). Measurements were usually taken up to more than 80% reaction. With decompositions of **21** in acetone-$d_6$ and acetonitrile-$d_3$, the rate constants are initial rates covering 40-45% reaction because of the upward drift as reported.[11] However, in DMF-$d_7$ no reported downward drift was observed up to more than 80% reaction. With **19** in acetone-$d_6$ (including some pyridine), an upward drift was observed for the points of more than 50% reaction.

**Acknowledgment.** The author is grateful to Drs. Shozo Masuda, Gaku Yamamoto, and Yohsuke Yamamoto for useful suggestions.

**Registry No. 1a**, 101225-70-1; **1b**, 101225-71-2; **1c**, 101225-72-3; **1d**, 101225-73-4; **1e**, 101225-74-5; **1f**, 101225-75-6; **1g**, 101225-76-7; **10**, 1203-13-0; **11**-$d_3$, 101225-77-8; **12**, 98-83-9; **14**, 101225-78-9; **15**, 617-94-7; **16**, 79490-50-9; **18a**, 101225-79-0; **18b**, 101225-80-3.

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# Azo Cope Rearrangement. A Sigmatropic Change Having a Strong Bias in the Direction of Heterolytic Bond Cleavage

**Tsutomu Mitsuhashi**

*Contribution from the Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.*

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**Abstract:** The first example of the azo Cope rearrangement is presented. Arylazo($\alpha,\alpha$-dimethylallyl)malononitriles are readily rearranged to *N*-($\gamma,\gamma$-dimethylallyl)arylhydrazonomalononitriles under mild conditions. The reaction rate increases greatly with increasing electron-withdrawing power of the substituent ($\log k/k_0 = 1.64\sigma$ in *o*-dichlorobenzene at 60 °C) and with increasing the basicity or nucleophilicity of the solvent, e.g., $CCl_4$ < acetone < methanol < pyridine < DMF < $Me_2SO$, indicating the polar structure of the transition state. A comparison of the kinetic behavior of the rearrangement with that of the carbon-carbon bond heterolysis of phenylazo-*tert*-cumylmalononitriles affords conclusive evidence for a concerted mechanism. The hydrogen-bond-insusceptible nature of polar sigmatropic reactions is discussed.

The electron-deficient azo system as a $\pi$ component in pericyclic reactions is unique in promoting electron transfer that increases the polar nature of the transition state, as can be seen from intensive work on the Diels-Alder reaction.[1] This paper presents the first example of the azo Cope rearrangement, i.e., the [3,3] sigmatropic shift involving an azo-to-hydrazone conversion which is exceedingly sensitive to the polar effects of substituents and solvents. The monoaza and diaza Cope rearrangements[2a-c] and

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monoaza Cope; X = Y = C

diaza Cope; X = N, Y = C

azo Cope; X = C, Y = N
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**Table I.** Kinetic Data for the Azo Cope Rearrangement

| compound | | in *o*-dichlorobenzene (DCB)[a] | | | | | | | | in methanol-$d_4$[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $10^5k$, $s^{-1}$, at | | | | | | | | $10^5k$, $s^{-1}$, at |
| **1** | X | 40 °C | 50 °C | 60 °C | 70 °C | 80 °C | 90 °C | $\Delta H^‡$, kcal/mol | $\Delta S^‡$, eu | 60 °C |
| **a** | *p*-$NO_2$ | 27.1 | 77.6 | 196 | 472 | 1200 | | 20.0 ± 0.6 | −11.2 ± 1.7 | 328[b] |
| **b** | *p*-CN | | 51.3 | 129 | 343 | 780 | | 20.1 ± 1.0 | −11.7 ± 3.0 | 228 |
| **c** | *m*-$NO_2$ | | 35.3 | 97.1 | 244 | 576 | | 20.4 ± 0.5 | −11.3 ± 1.4 | 172 |
| **d** | *m*-CN | | 28.4 | 74.5 | 199 | 470 | | 20.7 ± 0.7 | −11.0 ± 2.0 | 143 |
| **e** | *m*-Cl | | | 34.6 | 96.5 | 231 | 550 | 21.4 ± 0.9 | −10.4 ± 2.7 | 62.9 |
| **f** | *p*-Cl | | | 20.3 | 56.1 | 134 | 326 | 21.4 ± 0.8 | −11.3 ± 2.4 | 33.5 (32.5) |
| **g** | H | | | 11.2 | 32.4 | 76.3 | 188 | 21.7 ± 1.4 | −11.6 ± 3.9 | 18.4 (15.5) |
| **h** | *p*-Me | | | 5.74 | 15.5 | 36.2 | 92.5 | 21.4 ± 1.3 | −13.9 ± 3.6 | 9.93 (8.94) |
| **i** | *p*-MeO | | | 2.50 | 7.11 | 18.8 | 47.2 | 22.8 ± 0.2 | −11.2 ± 0.5 | 4.62 (3.74) |
| **j** | *o*-Cl | | | 48.7 | | | | | | 90.6 |
| **k** | 2,6-$Cl_2$ | | | 10.4 | | | | | | 19.8 (16.8) |

[a] The degree of conversion to **2**: in DCB, 95–98% (**1a–g**, **1j**), 90% (**1h**, **1i**), and 75% (**1k**), and in methanol-$d_4$, nearly quantitative (**1a–e**, **1j**); with others, **6** was formed as a byproduct, 3% (**1f**), 16% (**1g**), 10% (**1h**), 19% (**1i**), and 15% (**1k**), so that the rates were corrected by taking the yield of **6** into account as shown in parentheses. [b] $10^5k$, $s^{-1}$ (°C): 130 (50), 46.0 (40), 17.9 (31). $\Delta H^‡ = 19.6 \pm 0.4$ kcal/mol, $\Delta S^‡ = -11.2 \pm 1.4$ eu.

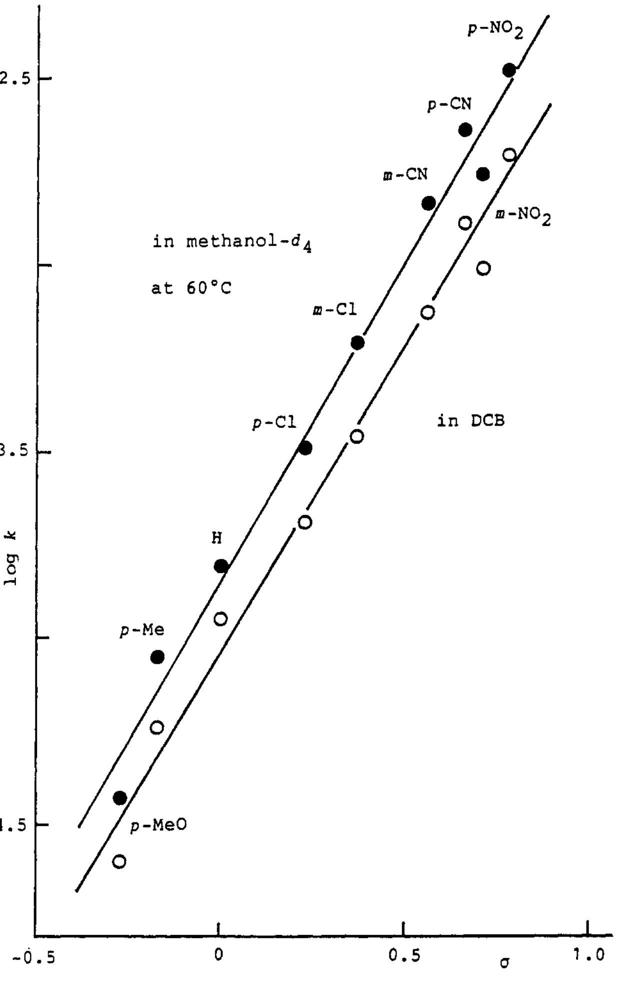
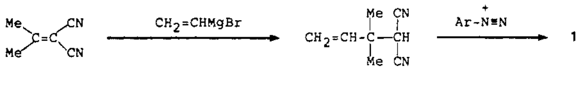


**Figure 1.** Plots of log *k* against *σ* for the azo Cope rearrangement.

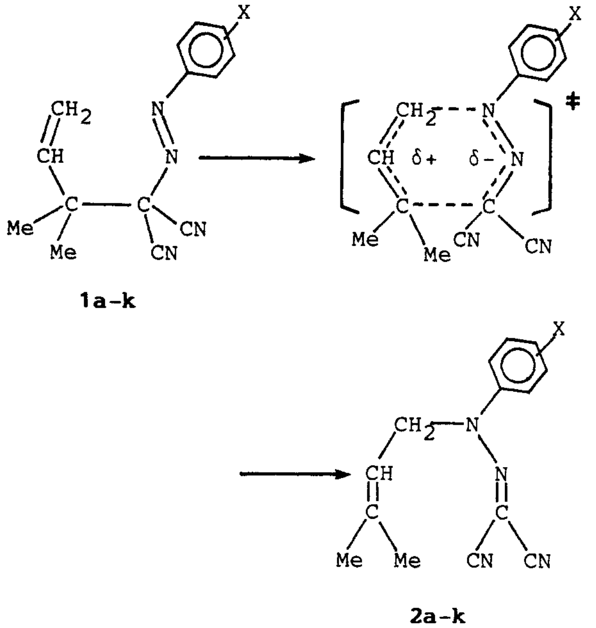
the rearrangement involving a hydrazone-to-azo conversion via a transient azo intermediate[3] have so far been reported. However, since the Cope rearrangement was discovered in 1940,[2d] the precedent for the azo Cope rearrangement had not as yet been reported, in contrast to the Diels–Alder reaction, the beginning of which was marked by the use of an azo compound.[4] The difficulty in achieving the azo Cope rearrangement lies in the fact that the usual azo compounds bearing an alkyl group, upon heating, easily suffer homolytic fission at the carbon–nitrogen bond. In the preceding paper,[5] we have demonstrated that arylazo-*tert*-alkylmalononitriles (**3**) undergo carbon–carbon bond heterolysis to generate the *tert*-alkyl cations **4** and the hydrazone anions **5**. The ease with which the bond cleavage occurs prompted us to investigate the thermal reactions of arylazo-*tert*-allylmalononitriles (**1**).

## Results and Discussion

**Products.** The azo compounds **1a–k** were prepared by coupling of the diazonium salts from substituted anilines to (*α*,*α*-dimethylallyl)malononitrile (**6**). The thermal rearrangement of **1a–k** to the hydrazones **2a–k** readily occurred under mild conditions; e.g., benzene solutions of **1a** (*p*-$NO_2$), **1g** (H), and **1i** (*p*-MeO) were maintained at 70 °C for periods of 0.5, 10, and 36 h, respectively, to produce the corresponding hydrazones, **2a** (95%), **2g** (94%), and **2i** (90%), which were isolated by TLC.



**6**



**1a–k**

**2a–k**

In general, the azo compounds bearing an electron-withdrawing group gave the hydrazones in excellent yields in any solvent. In cases of compounds without substituents, and with 2,6-dichloro and electron-donating substituents, however, the malononitrile **6** was formed in methanol as a byproduct resulting from a reversal of diazonium coupling (see footnote a in Table I).

**Substituent and Solvent Effects on Rate.** Kinetic measurements were made by following the changes in intensity of the methyl proton signals, and the first-order rate constants as well as the

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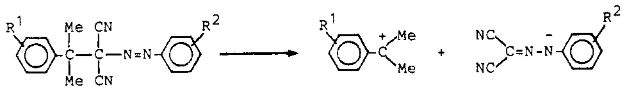
**Table II.** Solvent Effects on the Rate of Rearrangement of (*m*-Chlorophenyl)azo($\alpha,\alpha$-dimethylallyl)malononitrile at 60 °C

| solvent | $10^5k$, $s^{-1}$ | solvent | $10^5k$, $s^{-1}$ |
|---|---|---|---|
| $Me_2SO$-$d_6$ | 251 | acetone-$d_6$ | 59.8 |
| DMF-$d_7$ | 148 | DCB | 34.6 |
| $MeCN$-$d_3$ | 92.8 | $CDCl_3$ | 32.3 |
| pyridine | 86.4 | benzene | 31.9 |
| methanol-$d_4$ | 62.9 | $CCl_4$ | 13.2 |

activation parameters were obtained as summarized in Table I. The rate remarkably increases with increasing electron-withdrawing power of the substituent: The half-lifetime varies from 7.7 h (*p*-MeO) to 6 min (*p*-$NO_2$) in *o*-dichlorobenzene (DCB) at 60 °C. Plots of log ($k/k_0$) vs. the Hammett $\sigma$ values are linear with $\rho$ values of 1.64 ($R$ = 0.992) in DCB and 1.72 ($R$ = 0.993) in methanol-$d_4$ (Figure 1).[6] Evidently, the electronic effect is large compared to that expected from the isopolar character of the transition state for the usual sigmatropic reactions. The rate of rearrangement of the *m*-chloro derivative **1e** at 60 °C was examined in various solvents (Table II). The rate increases by a factor of 19 on changing from the nonpolar solvent $CCl_4$ to the dipolar solvent $Me_2SO$ which shows the strongest ionizing power among the solvents examined. It is interesting that the protic solvent methanol is less effective than the aprotic solvents $Me_2SO$ and DMF. A similar trend has been observed in the decomposition of the azo compound **3**.[5] These two effects clearly point to the polar structure of the transition state.

**Reaction Mechanism.** Two possible mechanisms are envisaged for the rearrangement, one proceeding via an ion pair ($S_N1'$) and the other concerted that may be expressed in terms of an intramolecular $S_N2'$ mechanism. The former mechanism resembles the decomposition of **3** in that it involves the rate-determining heterolysis of a carbon–carbon bond.[5] To probe the mechanism, the reactivity of **1a** was compared with that of **3a** in methanol. Striking features observed are as follows: (i) Conversion of **1a** to **2a** is nearly quantitative, no methanolysis products being detected. (ii) **1a** reacts faster than **3a** ($k_{1a}/k_{3a}$ = 3.4 at 60 °C, 6.7 at 31 °C), while the opposite situation is expected from the solvolysis data hitherto reported; e.g., the rate ratio of ethanolysis for the corresponding chlorides ($CH_2{=}CHCMe_2Cl$ vs. $PhCMe_2Cl$) is estimated to be 0.065 at 45 °C.[7,8] (iii) The **1a** → **2a** process exhibits a large negative $\Delta S^{\ddagger}$ value (−11.2 eu) compared to the methanolysis of **3a** (0.7 eu). Such an entropy loss seems inherent in the present rearrangement irrespective of the nature of solvents and substituents (see Table I) and contrasts markedly with an entropy gain ($\Delta S^{\ddagger}$ = 11–17 eu) reported for the carbon–nitrogen bond homolysis of the methyl analogues of **1** (Me instead of $CH_2{=}CHCMe_2$).[9] The results strongly suggest a concerted mechanism via a dipolar transition state in which partial charges are stabilized by a pericyclic interaction. Further evidence for the concerted mechanism comes from a free-energy relationship between the rates for **1a–d** and **3a–d** in methanol at 60 °C. The linear correlation obtained with $R$ = 0.995 reveals



**3** **4** **5**

| | $R^1$ | $R^2$ |
|---|---|---|
| a | H | *p*-$NO_2$ |
| b | H | *p*-CN |
| c | H | *m*-$NO_2$ |
| d | H | *m*-CN |
| e | *p*-MeO | H |
| f | *p*-MeO | *o*-Cl |
| g | *p*-MeO | 2,6-$Cl_2$ |

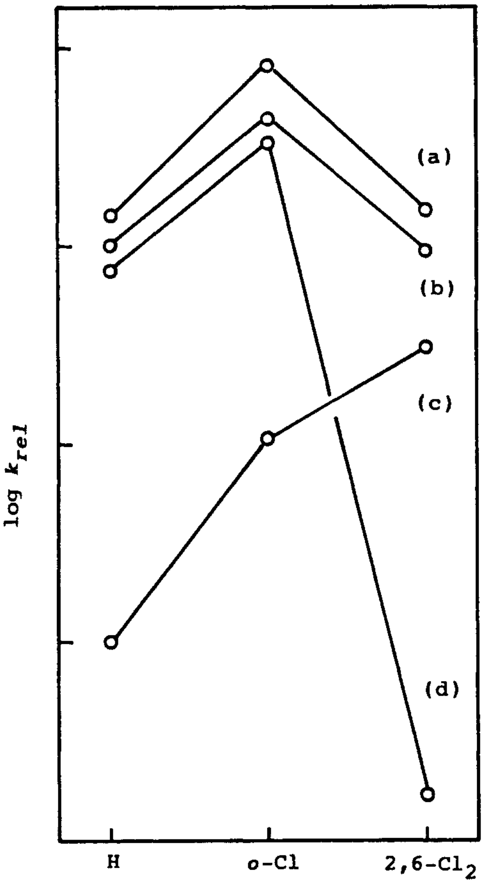


**Figure 2.** The ortho effect on rate. (a) **1** in methanol-$d_4$. (b) **1** in DCB. (c) **3** in 1:1 (v/v) benzene–methanol-$d_4$: $10^5k$, $s^{-1}$, at 31 °C; **3e**, 25.6; **3f**, 272; **3g**, 784. (d) ArCOCl + $PhNH_2$ (ref 10).

$$\log k_{1x} = 0.53 \log k_{3x} - 0.90$$

that **1** is more reactive but less sensitive to substituent changes than **3**, suggesting that a growing positive charge is stabilized to a certain extent by anchimeric assistance of the negatively charged azo nitrogen.

Another interesting feature is the ortho effect of chloro substituents. As illustrated in Figure 2, the rearrangement shows a propensity reminiscent of the ortho effect on the bimolecular reaction of benzoyl chlorides with aniline;[10] the first ortho substitution causes a rate enhancement due to an electronic effect of the chloro group, which however is canceled out by a steric effect upon the introduction of the second chloro group ($k_{1g}$:$k_{1j}$:$k_{1k}$ = 1:4.4:0.9 in DCB and 1:5.8:1.1 in methanol-$d_4$ at 60 °C). On the other hand, the methanolysis rates of **3e**, **3f**, and **3g** indicate that the accelerative effect is cumulative to an extent of the ratio 1:11:31 in 1:1 (v/v) benzene–methanol-$d_4$ at 31 °C. A similar cumulative effect of ortho substituents has been reported for the ethanolysis of methyl-substituted 1-phenylethyl chlorides.[11] Thus the observed steric retardation in **1k** provides conclusive evidence for carbon–nitrogen bond forming in the transition state and definitely excludes an ion-pair mechanism.[12]

The electronic structure of the transition state, which may be best visualized as the cyclic interaction between antisymmetric molecular orbitals of allyl and diazaallyl fragments,[13-15] not only

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[6] $\sigma$ values are taken from ref 23. With **1c** (*m*-$NO_2$), some rate depression appears as has been observed in the decomposition of **3c**.[5] The substituent effect on rates of the Cope rearrangement of 2-aryl-1,5-hexadienes has been reported. Although this sytem seems inadequate for the purpose of comparison because the aryl group is located at the 2-position, the effect is small and shows a concave Hammett plot: Marvell, E. N.; Li, T.-C. *J. Am. Chem. Soc.* **1978**, *100*, 883.

[7] Vernon, C. A. *J. Chem. Soc.* **1954**, 4462.

[8] Smith, S. G.; Goon, D. J. W. *J. Org. Chem.* **1969**, *34*, 3127.

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[10] Mather, J. G.; Shorter, J. *J. Chem. Soc.* **1961**, 4744.

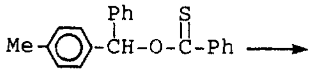
[11] Charlton, J. C.; Hughes, E. D. *J. Chem. Soc.* **1956**, 850.

[12] The reversible formation of the ion pair, by which the steric effect might be explained, is least likely to occur as discussed in the preceding paper.[5]

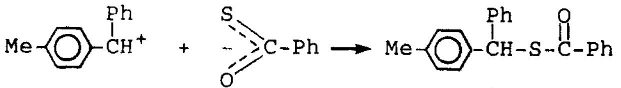
satisfies essential requirements of orbital symmetry of the "normal" Diels–Alder reaction[16,17] but, compared with the HOMO–LUMO interaction in the azo Diels–Alder reaction, can effect great charge separation as a result of predominating electron transfer to the lower-lying orbital of the two. There are two a priori extremes in pericyclic reactions; one is located near the borderline of homolysis, and the other near the borderline of heterolysis. The former extreme has already been studied intensively in the Cope rearrangement.[18] To the best of our knowledge, the present work provides the first and pertinent example of the latter case.

**Hydrogen-Bond-Insusceptible Nature of Polar Sigmatropic Reactions.** In the preceding paper,[5] we put forward a fundamental proposal that polar unimolecular reactions can be classified into two types with respect to the differential solvation, and the $P_s$ value (the difference in the free energy of activation between the reactions in methanol and in $Me_2SO$) was introduced to classify the reaction. The $S_N1$–E1 reactions to generate hydrazone anions **5** exhibit positive $P_s$ values ($k_{Me_2SO} > k_{methanol}$) because of extensive negative charge delocalization that prevents hydrogen bonding with a protic solvent molecule. We termed them hydrogen-bond-insusceptible reactions in contrast to the hydrogen-bond-stabilized reactions which generate halide and sulfonate ions with negative $P_s$ values.

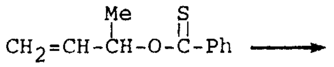
As described above, the rearrangement of **1e** to **2e** shows a positive $P_s$ value (0.9 kcal/mol at 60 °C), and hence the mode of such a rearrangement suggests another approach to the hydrogen-bond-insusceptible reactions, which involves a cation-induced intramolecular blocking effect on the anionic site where a hydrogen bond would otherwise be formed. It has turned out that the rearrangements of the thionbenzoates **7a–b** to the thiolbenzoates **8a–b** reported by Smith[19,20] are exactly what have been intended for a demonstration (Table III). Conversion of



**7a**

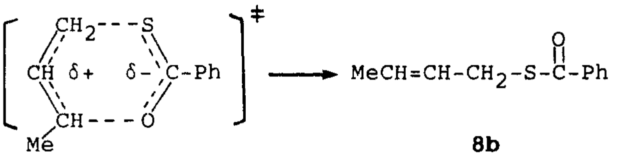


**8a**



$CH_2{=}CH{-}CH(Me){-}O{-}C({=}S){-}Ph \longrightarrow$

**7b**



**8b**

**7a** to **8a** takes place via an ion pair as is evidenced by the fact that it competes with solvolysis in ethanol.[19] On the other hand, **7b** yields **8b** exclusively in any solvent, and it has been suggested from the lower sensitivity to solvent polarity that charge separation in the transition state is relatively small.

**Table III.** Kinetic Data on the Rearrangements of Thionbenzoates **7a** and **7b**

| | $10^5k$, $s^{-1}$ | |
|---|---|---|
| | **7a** (85 °C)[a] | **7b** (60 °C)[b] |
| methanol-$d_4$ | 205[c] | 6.18[e] |
| $\Delta H^‡$, kcal/mol | 23.7 ± 0.7 | 23.3 ± 0.9 |
| $\Delta S^‡$, eu | −5.0 ± 2.1 | −7.9 ± 2.6 |
| $Me_2SO$-$d_6$ | 24.8[d] | 13.7[f] |
| $\Delta H^‡$, kcal/mol | 25.6 ± 0.9 | 21.7 ± 0.8 |
| $\Delta S^‡$, eu | −4.0 ± 2.4 | −11.3 ± 2.2 |
| MeCN-$d_3$ | 18.8 | 7.26 |
| DMF-$d_7$ | 7.73 | 7.52 |
| pyridine | 3.96[g] | 5.38 |
| acetone-$d_6$ | 1.20[h] | 3.72 |

[a] Rates of formation of **8a** based on the methine proton signal. [b] Consumption rates of **7b** based on the methyl proton signal. [c] $10^5k$, $s^{-1}$ (°C): 8.92 (55), 26.0 (65), 74.1 (75). [d] 2.71 (65), 8.20 (75), 64.6 (95). [e] 18.6 (70), 50.0 (80), 124 (90). [f] 38.4 (70), 93.9 (80), 226 (90). [g] In pyridine-$d_5$. [h] Including pyridine-$d_5$ in amounts equimolar with **7a**.

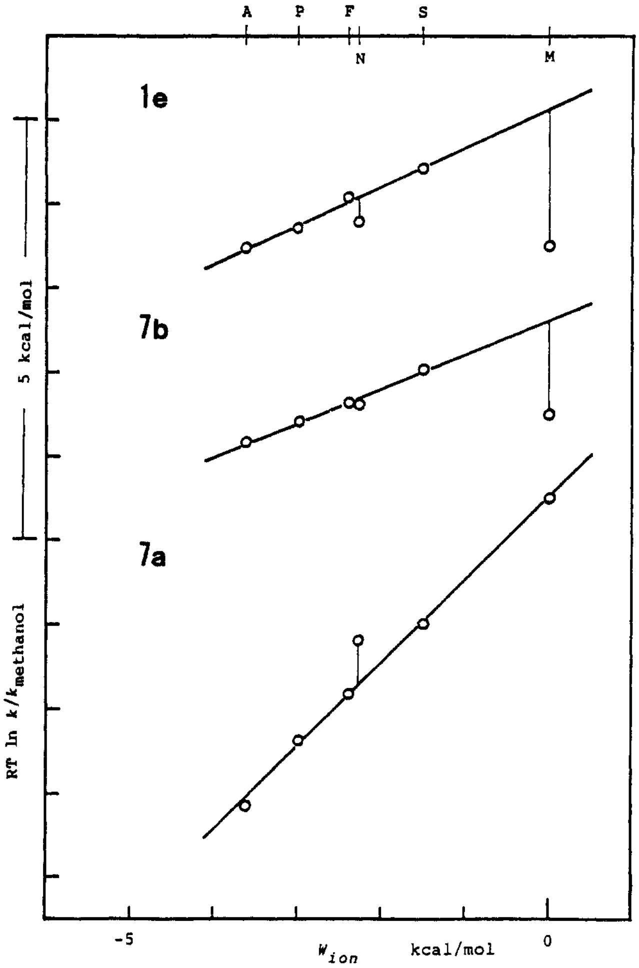


Figure 3. Plots of $-\Delta\Delta G^*$ vs. $W_{ion}$ and the APFS line. Solvents: A = acetone; P = pyridine; F = DMF; N = MeCN; S = $Me_2SO$; M = methanol. **1e**, 60 °C, slope = 0.46 ($R$ = 0.996, the correlation coefficient of the APFS line); **7b**, 60 °C, slope = 0.41 ($R$ = 0.999); **7a**, 85 °C, slope = 1.00 ($R$ = 0.994).

For the present purpose, we examined the solvent effects on the rates of these reactions in further detail. From the rate constants summarized in Table III, it is evident that the rearrangement of **7a** is stabilized by hydrogen bonding with a $P_s$ value of −1.5 kcal/mol (at 60 °C). In sharp contrast, with **7b**, the $P_s$ value has turned positive (0.5 kcal/mol at 60 °C). The results together with the $\Delta S^*$ value observed are consistent with a concerted mechanism. It would be necessary to take it into account that the rearrangement owes its hydrogen-bond-insusceptible property partly to the desolvation energy required to break the

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hydrogen bond between **7b** and methanol present in the initial state.

Figure 3 shows that the APFS line (the straight line composed of the points for acetone, pyridine, DMF, and $Me_2SO$) holds good for plots of $RT \ln k/k_{\text{methanol}}$ vs. $W_{\text{ion}}$ $(=RT \ln k_{\text{ion}}/k_{\text{ion,methanol}})$ in all the rearrangements of the azo compound **1e** and the thionbenzoates **7a–b** similarly as has been seen in $S_N1$–E1 reactions. Accordingly, the result further supports the view that cation solvation manifested as the slope of the APFS line has nothing to do with $S_N2$-like attack by a solvent molecule, since **1e** and **7b** afford none of the solvolysis products. The plots for **1e** and **7b** have a close analogy with those for the hydrogen-bond-insusceptible $S_N1$–E1 reactions.[5]

It would therefore be predicted that the hydrogen-bond-insusceptible nature might be a general phenomenon in the polar sigmatropic reactions of this sort. On the basis of these observations together with the parallel results and discussion reported in the preceding paper, we might expect it a general rule that as far as solvent–solute interactions other than hydrogen bonding are concerned, dipolar aprotic solvents such as $Me_2SO$ and DMF possess the ability to stabilize dipolar species more effectively than protic solvents represented by methanol, and the differences in solvation seem to stem mainly from basic or nucleophilic properties of solvents.

## Conclusion

It has been established from the present and preceding papers[5] that arylazoalkylmalononitriles are able to cause four different kinds of thermal unimolecular reactions depending on the nature of the alkyl and aryl groups: (i) carbon–nitrogen bond homolysis reported in the literature;[9] (ii) carbon–nitrogen bond heterolysis, i.e., a reversal of diazonium coupling; (iii) carbon–carbon bond heterolysis;[5] (iv) the azo Cope rearrangement involving synchronous carbon–carbon bond cleavage and carbon–nitrogen bond formation presented herein. The rearrangement proceeds via the dipolar transition state, and the examination of differential solvation reveals the hydrogen-bond-insusceptible nature of the rearrangement. Likewise, the rearrangement of α-methylallyl thionbenzoate, examined as another example of the polar [3,3]-sigmatropic shift, also behaves as a reaction of this type, contrary to the hydrogen-bond-susceptible character of the rearrangement of *p*-methylbenzhydryl thionbenzoate via an ion-pair intermediate.

## Experimental Section

General conditions were described in the preceding paper.[5]

**(α,α-Dimethylallyl)malononitrile (6).** To a vigorously stirred and water-cooled solution of vinylmagnesium bromide in 70 mL of THF prepared from 25 mL (0.35 mol) of vinyl bromide and 8.4 g of magnesium was added a solution of 27 g (0.25 mol) of 1,1-dicyano-2-methylpropene[21] in 50 mL of THF under nitrogen. A gummy precipitate, which was deposited very soon, disturbed efficient stirring and resulted in low yield of **6**. Benzene (50 mL) was introduced, and the stirring was continued for 1 h. After treated with aqueous $NH_4Cl$ solution, the organic layer was dried ($MgSO_4$) and freed of solvent. Repetition of distillation gave 14 g of colorless liquid (bp 87–89 °C/5 mmHg) which was a mixture of **6** and the starting propene (60:40). To the liquid was added 15 mL of piperidine and the mixture was stirred for 30 min. The orange solution was poured onto ice-cooled dilute HCl and extracted with $CH_2Cl_2$. The organic layer was washed with dilute HCl and then with water and dried. Solvent evaporation gave a mixture of a liquid and a colorless solid, which was then extracted with benzene, and the extract was subjected to distillation (twice) to give 7.2 g (17%) of **6**: bp 68 °C/2 mmHg; NMR δ 1.38 (s, 6 H), 3.50 (s, 1 H), 5.15–6.06 (m, 3 H). Anal. Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.32; H, 7.47; N, 20.97.

**Arylazo(α,α-dimethylallyl)malononitriles (1).** The procedure described in the preceding paper[5] was employed for diazonium coupling to **6**. The crude product was dissolved in hexane or $CH_2Cl_2$ and chromatographed on silica gel (eluent: hexane or hexane–$CH_2Cl_2$) at 10–15 °C, especially at 0 °C for **1a–e** and **1j**. The eluate of a yellow band was collected and concentrated at 0 °C in vacuo, and the residue was recrystallized repeatedly from hexane or hexane–$CH_2Cl_2$ at −20 °C, except for **1j** which resisted crystallization and was purified with TLC (Merk Kieselgel Art. 5717) at −20 °C. All the compounds are yellow. Unstable azo compounds were stored at dry ice temperature, and elemental analyses were performed immediately after the samples were allowed to warm to room temperature. Some of them quickly rearrange to **2** during melting point measurements. **1a** (*p*-$NO_2$): mp 81 °C; NMR δ 1.52 (s, 6 H), 5.2–6.2 (m, 3 H), 7.98 (d, *J* = 9 Hz, 2 H), 8.42 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{14}H_{13}N_5O_2$: C, 59.35; H, 4.63; N, 24.72. Found: C, 59.58; H, 4.61; N, 24.52. **1b** (*p*-CN): mp 77 °C; NMR δ 1.51 (s, 6 H), 5.2–6.2 (m, 3 H), 7.8–8.05 (m, 4 H). Anal. Calcd for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60. Found: C, 68.60; H, 4.90; N, 26.57. **1c** (*m*-$NO_2$): mp 86 °C; NMR δ 1.51 (s, 6 H), 5.2–6.2 (m, 3 H), 7.67–8.67 (m, 4 H). Anal. Calcd for $C_{14}H_{13}N_5O_2$: C, 59.35; H, 4.63; N, 24.72. Found: C, 59.62; H, 4.49; N, 24.74. **1d** (*m*-CN): mp 72 °C; NMR δ 1.50 (s, 6 H), 5.2–6.2 (m, 3 H), 7.55–8.18 (m, 4 H). Anal. Calcd for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60. Found: C, 68.44; H, 4.91; N, 26.85. **1e** (*m*-Cl): mp 46 °C; NMR δ 1.50 (s, 6 H), 5.2–6.2 (m, 3 H), 7.44–7.86 (m, 4 H). Anal. Calcd for $C_{14}H_{13}ClN_4$: C, 61.65; H, 4.80; N, 20.54. Found: C, 61.73; H, 4.67; N, 20.74. **1f** (*p*-Cl): mp 43 °C; NMR δ 1.49 (s, 6 H), 5.2–6.2 (m, 3 H), 7.51 (d, *J* = 9 Hz, 2 H), 7.80 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{14}H_{13}ClN_4$: C, 61.65; H, 4.80; N, 20.54. Found: C, 61.74; H, 4.77; N, 20.66. **1g** (H): mp 26 °C; NMR δ 1.48 (s, 6 H), 5.2–6.2 (m, 3 H), 7.4–7.9 (m, 5 H); IR ($cm^{-1}$) 2250 (vw, CN). Anal. Calcd for $C_{14}H_{14}N_4$: C, 70.56; H, 5.92; N, 23.51. Found: C, 70.45; H, 5.67; N, 23.28. **1h** (*p*-Me): mp 19 °C; NMR δ 1.47 (s, 6 H), 2.42 (s, 3 H), 5.2–6.2 (m, 3 H), 7.28 (d, *J* = 8 Hz, 2 H), 7.70 (d, *J* = 8 Hz, 2 H). Anal. Calcd for $C_{15}H_{16}N_4$: C, 71.40; H, 6.39; N, 22.21. Found: C, 71.60; H, 6.09; N, 22.26. **1i** (*p*-MeO): mp 67 °C; NMR δ 1.47 (s, 6 H), 3.89 (s, 3 H), 5.2–6.2 (m, 3 H), 6.98 (d, *J* = 9 Hz, 2 H), 7.82 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{15}H_{16}N_4O$: C, 67.14; H, 6.01; N, 20.88. Found: C, 67.30; H, 6.06; N, 20.96. **1j** (*o*-Cl): oil; NMR δ 1.50 (s, 6 H), 5.2–6.2 (m, 3 H), 7.2–7.7 (m, 4 H). Anal. Calcd for $C_{14}H_{13}ClN_4$: C, 61.65; H, 4.80; N, 20.54. Found: C, 61.45; H, 4.73; N, 20.55. **1k** (2,6-$Cl_2$): mp 74 °C; NMR δ 1.51 (s, 6 H), 5.25–6.23 (m, 3 H), 7.15–7.52 (m, 3 H). Anal. Calcd for $C_{14}H_{12}Cl_2N_4$: C, 54.74; H, 3.94; N, 18.24. Found: C, 54.53; H, 3.90; N, 18.25.

**Rearrangements of 1.** A solution of 0.6 mmol of **1** in 3 mL of benzene was heated at 70 °C. After the reaction was complete, the crude product was purified by TLC (eluent: $CH_2Cl_2$). According to this procedure, the yield was determined for three substrates (**1a**, **1g**, and **1i**) as described in the text. The yield listed in Table I (footnote) was determined by NMR measurements using a measured amount of an internal standard. The hydrazones **2** were further purified by recrystallization from ethanol or benzene–hexane for the solid mass and are tinged with yellow unless otherwise noted. **2a**: mp 85.5 °C; NMR δ 1.77 (s, 3 H), 1.83 (s, 3 H), 4.99 (d, *J* = 6 Hz, 2 H), 5.21 (t, *J* = 6 Hz, 1 H), 7.48 (d, *J* = 10 Hz, 2 H), 8.27 (d, *J* = 10 Hz, 2 H). Anal. Calcd for $C_{14}H_{13}N_5O_2$: C, 59.34; H, 4.63; N, 24.72. Found: C, 59.37; H, 4.45; N, 24.98. **2b**: mp 112 °C; NMR δ 1.73 (s, 3 H), 1.82 (s, 3 H), 4.92 (d, *J* = 6 Hz, 2 H), 5.19 (t, *J* = 6 Hz, 1 H), 7.41 (d, *J* = 9 Hz, 2 H), 7.70 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60. Found: C, 68.32; H, 4.76; N, 26.52. **2c**: mp 52 °C; NMR δ 1.73 (s, 3 H), 1.81 (s, 3 H), 4.91 (d, *J* = 6 Hz, 2 H), 5.25 (t, *J* = 6 Hz, 1 H), 7.5–8.3 (m, 4 H). Anal. Calcd for $C_{14}H_{13}N_5O_2$: C, 59.34; H, 4.63; N, 24.72. Found: C, 59.04; H, 4.51, N, 24.53. **2d**: oil; NMR δ 1.70 (s, 3 H), 1.80 (s, 3 H), 4.82 (d, *J* = 6 Hz, 2 H), 5.20 (t, *J* = 6 Hz, 1 H), 7.4–7.7 (m, 4 H). Anal. Calcd for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60. Found: C, 68.31; H, 4.69; N, 26.81. **2e**: oil; NMR δ 1.65 (s, 3 H), 1.80 (s, 3 H), 4.74 (d, *J* = 6 Hz, 2 H), 5.22 (t, *J* = 6 Hz, 1 H), 7.05–7.45 (m, 4 H). Anal. Calcd for $C_{14}H_{13}ClN_4$: C, 61.65; H, 4.80; N, 20.54. Found: C, 61.46; H, 5.01; N, 20.64. **2f**: 76 °C; NMR δ 1.61 (s, 3 H), 1.79 (s, 3 H), 4.70 (d, *J* = 6 Hz, 2 H), 5.24 (t, *J* = 6 Hz, 1 H), 7.17 (d, *J* = 9 Hz, 2 H), 7.40 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{14}H_{13}ClN_4$: C, 61.65; H, 4.80; N, 20.54. Found: C, 61.53; H, 4.56; N, 20.38. **2g**: mp 73 °C; NMR δ 1.59 (s, 3 H), 1.78 (s, 3 H), 4.67 (d, *J* = 6 Hz, 2 H), 5.29 (t, *J* = 6 Hz, 1 H), 7.1–7.6 (m, 5 H); IR ($cm^{-1}$) 2220 (s, CN), 2200 (m, CN). Anal. Calcd for $C_{14}H_{14}N_4$: C, 70.56; H, 5.92; N, 23.51. Found: C, 70.34; H, 5.63; N, 23.25. **2h**: mp 75 °C; NMR δ 1.53 (s, 3 H), 1.73 (s, 3 H), 2.39 (s, 3 H), 4.58 (d, *J* = 7 Hz, 2 H), 5.25 (t, *J* = 7 Hz, 1 H), 7.05 (d, *J* = 9 Hz, 2 H), 7.23 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{15}H_{16}N_4$: C, 71.40; H, 6.39; N, 22.21. Found: C, 71.11; H, 6.27; N, 22.01. **2i**: mp 54 °C; NMR δ 1.53 (s, 3 H), 1.75 (s, 3 H), 3.83 (s, 3 H), 4.50 (d, *J* = 7 Hz, 2 H), 5.28 (t, *J* = 7 Hz, 1 H), 6.89 (d, *J* = 9 Hz, 2 H), 7.09 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{15}H_{16}N_4O$: C, 67.14; H, 6.01; N, 20.88. Found: C, 67.15; H, 5.73; N, 20.76. **2j**: oil; NMR δ 1.50 (s, 3 H), 1.73 (s, 3 H), 4.48 (d, *J* = 7.5 Hz, 2 H), 5.31 (t, *J* = 7.5 Hz, 1 H), 7.1–7.6 (m, 4 H). Anal. Calcd for $C_{14}H_{13}ClN_4$: C, 61.65; H, 4.80; N, 20.54. Found: C, 61.65; H, 4.58; N, 20.25. **2k** (colorless prisms): mp 60 °C; NMR δ 1.53 (s, 3 H), 1.71 (s, 3 H), 4.54 (d, *J* = 7.5 Hz, 2 H), 5.39 (t, *J* = 7.5 Hz, 1 H), 7.3–7.5 (m, 3 H). Anal. Calcd

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J. Am. Chem. Soc. 1986, 108, 2405–2408

for $C_{14}H_{12}Cl_2N_4$: C, 54.74; H, 3.94; N, 18.24. Found: C, 55.03; H, 4.20; N, 18.14.

**Arylazo(α,α-dimethyl-*p*-methoxybenzyl)malononitriles (3e–g).** The azo compounds **3e–g** were prepared by the reaction of diazotized anilines with (α,α-dimethyl-*p*-methoxybenzyl)malononitrile which was obtained from methylmagnesium iodide and 1,1-dicyano-2-(*p*-methoxyphenyl)-propene.[22] These were recrystallized from benzene–hexane to afford yellow prisms, which underwent methanolysis very rapidly when dissolved in methanol. **3e**: mp 77 °C; NMR $\delta$ 1.83 (s, 6 H), 3.77 (s, 3 H), 6.82 (d, $J$ = 9 Hz, 2 H), 7.39 (d, $J$ = 9 Hz, 2 H), 7.4–7.85 (m, 5 H). Anal. Calcd for $C_{19}H_{18}N_4O$: C, 71.68; H, 5.70; N, 17.60. Found: C, 71.89; H, 5.70; N, 17.50. **3f**: mp 81 °C; NMR $\delta$ 1.83 (s, 6 H), 3.78 (s, 3 H), 6.84 (d, $J$ = 9 Hz, 2 H), 7.40 (d, $J$ = 9 Hz, 2 H), 7.2–7.7 (m, 4 H). Anal. Calcd for $C_{19}H_{17}ClN_4O$: C, 64.68; H, 4.86; N, 15.88. Found: C, 64.62; H, 5.04; N, 15.87. **3g**: mp 83 °C; NMR $\delta$ 1.88 (s, 6 H), 3.78 (s, 3 H), 6.87 (d, $J$ = 9 Hz, 2 H), 7.50 (d, $J$ = 9 Hz, 2 H), 7.2–7.4 (m, 3 H). Anal. Calcd for $C_{19}H_{16}Cl_2N_4O$: C, 58.93; H, 4.16; N, 14.47. Found: C, 58.97; H, 4.45; N, 14.60.

**Thionbenzoates 7a and 7b.** The thionbenzoates were prepared according to the literature procedure.[19,20] **7a** (yellowish-orange oil): NMR $\delta$ 2.32 (s, 3 H), 7.0–7.6 (m, 12 H), 7.75 (s, 1 H), 8.15–8.35 (m, 2 H). **7a** gave **8a** exclusively in aprotic solvents except pyridine. The pyridiniuim salt, which showed characteristic signals in the aromatic region of the NMR spectrum, was formed in the ratio of the salt to **8a** of ca. 40:60 in pyridine-$d_5$ at 85 °C. **7a** gave ca. equal amounts of **8a** and the substitution product in methanol-$d_4$. **8a** (colorless prisms): mp 73 °C; NMR $\delta$ 2.31 (s, 3 H), 6.11 (s, 1 H), 6.95–7.5 (m, 12 H), 7.85–8.05 (m, 2 H). **7b** (yellowish-orange oil): NMR $\delta$ 1.53 (d, $J$ = 6 Hz, 3 H), 5.1–6.4 (m, 4 H), 7.2–7.6 (m, 3 H), 8.1–8.3 (m, 2 H). **7b** was converted to **8b** nearly quantitatively in any solvent. **8b** (colorless oil): NMR $\delta$ 1.4–1.8 (m, 3 H), 3.65 (d, $J$ = 6 Hz, 2 H), 5.25–6.0 (m, 2 H), 7.2–7.6 (m, 3 H), 7.8–8.1 (m, 2 H).

**Kinetics.** Kinetic experiments were carried out as described in the preceding paper.[5] The rates of rearrangement and solvolysis were determined by following the decrease of the methyl peak on the allyl or phenyl group except for the cases of **1j** and **7a**, in which the increase of the methyl peak of **2j** and the methine peak of **8a** was monitored. 9,10-Dihydroanthracene, anisole, *p*-xylene, or *p*-nitrotoluene was used as an internal standard.

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# Structure and Electronic Nature of the Benzaldehyde/Boron Trifluoride Adduct

**M. T. Reetz,*[†] M. Hüllmann,[†] W. Massa,[†] S. Berger,[†] P. Rademacher,[‡] and P. Heymanns[‡]**

*Contribution from the Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse, 3550 Marburg, FRG, and the Institut für Organische Chemie, Universität Essen, 4300 Essen, FRG.*

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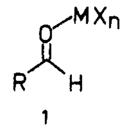
**Abstract:** The structure of the benzaldehyde/boron trifluoride adduct (**6**) has been determined by X-ray crystallography. Accordingly, the Lewis acid $BF_3$ is complexed anti to the phenyl group in benzaldehyde. The B–O–C–C fragment lies essentially in a common plane. Anti complexation also pertains in solution, as shown by a heteronuclear Overhauser experiment. MNDO calculations of the acetaldehyde/$BF_3$ adduct show that anti complexation does indeed lead to the lowest energy species. However, the syn adduct lies only 1.8 kcal/mol higher in energy. The linear form does not represent a minimum on the energy surface but rather the lowest energy transition state for intramolecular anti $\rightleftarrows$ syn isomerization. The calculations of $CH_3CHO/BF_3$, of **6**, and of the free aldehydes clearly point to LUMO lowering and to an increased positive charge at the carbonyl carbon atom upon complexation. The results are discussed in light of Lewis acid mediated aldehyde additions involving allyl and enolsilanes, stannanes, and cyanotrimethylsilane as well as such processes as Diels–Alder, ene, and Grignard reactions.

A wide variety of C–C bond-forming reactions of carbonyl compounds are mediated by Lewis acids such as $BF_3$, $AlCl_3$, $EtAlCl_2$, $TiCl_4$, $SnCl_4$, and $ZnX_2$. They include carbonyl additions of allylsilanes, enosilanes, cyanotrimethylsilane, and other silyated[1] and stannylated[2] carbon nucleophiles, as well as ene reactions,[3] Diels–Alder additions,[4] and hetero-Diels–Alder cyclocondensations.[5] It is generally accepted that the Lewis acid activates the carbonyl component by forming an adduct prior to C–C bond formation.

Whereas X-ray crystallographic data of a $TiCl_4$ adduct of a chiral acrylic acid ester has recently been reported and discussed with regard to stereoselective Diels–Alder reactions,[6] precise structural information concerning complexes of aldehydes with the above-mentioned Lewis acid remains to be presented. NMR, UV, and IR data of common aldehyde/Lewis acid complexes are available, but they do not answer the question of anti vs. syn complexation (**1** vs. **2**; $MX_n$ = Lewis acid).[7] A great deal of experimental and theoretical work concerning the interaction of formaldehyde with $Li^+$ and other Lewis acids has accumulated over the years.[8,9] For example, the geometries and energies of complexes between $CH_2O$ and first- and second-row cations such



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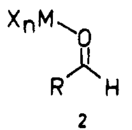

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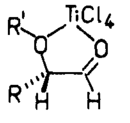

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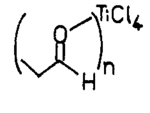

4 (n=1,2)

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[†] Philipps-Universität.

[‡] Universität Essen.

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