# *Communications*

## Reversal of Electronic Substituent Effects in the Retro-Diels–Alder Reaction. A Charge Neutral Analogue of Oxyanion-Accelerated Cycloreversion

*Summary:* The retro-Diels–Alder reaction of anthracene cycloadducts is influenced by dienophile substituents in the following ways: (1) electron-withdrawing groups increase the rate of the reaction; (2) strongly conjugating substituents make the reaction *much* faster than predicted by classical electron-withdrawing or -donating ability, in the best case by a factor of $3 \times 10^6$, and (3) there is *no* observable steric effect, in contrast to literature statements to the contrary.

*Sir:* The retro-Diels–Alder (rDA) reaction is a $\pi^2s + \sigma^2s + \sigma^2s$ electrocyclic process that, as the name implies, is the reverse of the familiar Diels–Alder cycloaddition reaction.[1,2] While the factors that influence the rate of the cycloaddition reaction are rather well established, there remains little predictive ability in knowing at what temperature a cycloreversion will occur. Surprisingly, a systematic study of the substituent effect on the retro-Diels–Alder reaction has never been reported; such information is essential to our group's work on the design of cycloaddition/cycloreversion-based catalysts.[3] In addition, recent syntheses in which retro-Diels–Alder reactions played a key role[4] point to the need to understand how these reactions can be done at less than pyrolytic temperatures. In 1967, Hart[5] reported what is likely one of the first examples of an oxyanion-accelerated rDA reaction. Since the recognition by Evans[6] that the Cope rearrangement is subject to alkoxide-acceleration by a factor of up to $10^{17}$, acceleration of the rDA reaction by both oxyanionic[4a,7–9] and carbanionic[10,11] substituents has been documented.

We now report that, like the forward Diels–Alder reaction, electron-withdrawing groups on the dienophile fragment accelerate the retro-Diels–Alder process; however, *conjugating substituents can accelerate the reaction even if strongly electron donating*, in analogy to the effect ob-
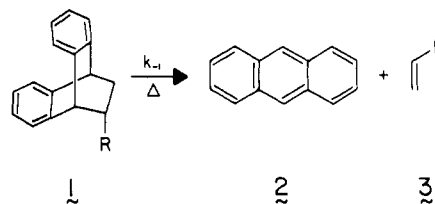


**Figure 1.**

served with oxyanionic substituents.[8]

Adducts between anthracene and substituted ethylenes were prepared either by direct cycloaddition or by functional group conversion of a known adduct;[12] all compounds used for kinetic runs were of microanalytical purity.[13a] In each case, cycloreversion (Figure 1) was accomplished by heating a $1.14 \times 10^{-4}$ M solution of the adduct in diphenyl ether in a sealed ampule at $250 \pm 0.5$ °C.[13b] The first-order rate constants[14] for the reactions are shown in Table I, from which several patterns emerge. First, there seems to be no steric effect, as evidenced by the fact that all the simple alkyl derivatives (**1b–e**) cyclorevert at essentially the same rate. Molecular mechanics calculations[14] predict that the most stable conformations of these compounds will be relieved of 0.37 (Me), 0.36 (Et), 1.1 (*i*-Pr), and 2.3 (*t*-Bu) kcal/mol more strain energy than will the H-substituted adduct (**1a**) on cycloreversion; this ordering, as well as being computationally rigorous, is consistent with intuition. Our finding is in stark contrast to the known steric effect in the cycloaddition direction; increasingly bulky substituents make the forward Diels–Alder reaction progressively slower.[15] This dichotomy is satisfactorily rationalized by recalling that the Diels–Alder reaction has a "late" transition structure, which closely resembles the adduct.[16] Conversely, the retro-Diels–Alder reaction has an "early" transition structure; the strain energy stored in the adduct is felt equally by the transition structure, and so its eventual release comes too late to provide a rate acceleration. It therefore seems likely that some past citings of strain-accelerated retro-Diels–Alder processes must be reattributed to other effects.

(1) For synthetic reviews of the retro-Diels–Alder reaction, see: (a) Ripoll, J.-L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19. (b) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 229. (c) Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415. (d) Lasne, M.-C.; Ripoll, J.-L. *Synthesis* **1985**, 121.

(2) For mechanistic reviews of the retro-Diels–Alder reaction, see: (a) Reference 1c. (b) Smith, G. G.; Kelly, F. W. *Prog. Phys. Org. Chem.* **1971**, *8*, 201. (c) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(3) Czarnik, A. W. *Tetrahedron Lett.* **1984**, *25*, 4875.

(4) For example, see: (a) Knapp, S.; Ornaf, R. M.; Rodriques, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 5494. (b) Kodpinid, M.; Siwapinyoyos, T.; Thebtaranonth, Y. *J. Am. Chem. Soc.* **1984**, *106*, 4862. (c) Anderson, W. K.; Milowsky, A. S. *J. Org. Chem.* **1985**, *50*, 5423. (d) Magnus, P.; Cairns, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 217.

(5) Oku, A.; Kakihana, T.; Hart, H. *J. Am. Chem. Soc.* **1967**, *89*, 4554.

(6) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.

(7) Papies, O.; Grimme, W. *Tetrahedron Lett.* **1980**, *21*, 2799.

(8) Rajanbabu, T. V.; Eaton, D. F.; Fukunaga, T. *J. Org. Chem.* **1983**, *48*, 652.

(9) VaraPrasad, J. V. N.; Iyer, P.; Pillai, C. N. *J. Org. Chem.* **1982**, *47*, 1380 (see the criticism of this paper in ref 8).

(10) Bowman, E. S.; Hughes, G. B.; Grutzner, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 8273.

(11) Papies, O.; Grimme, W. *Tetrahedron Lett.* **1978**, 2201.

(12) Complete syntheses for these structurally simple compounds will be presented in the full paper.

(13) (a) All compounds were analyzed for elements other than oxygen, with agreement to within 0.4% in each case. Microanalyses were carried out at Canadian Microanalytical Service, New Westminster, B.C.; (b) At various times, an ampule was cooled to room temperature, opened, and the concentration of anthracene was determined by measuring the solution's absorbance at 362 nm, at which diphenyl ether is essentially transparent.

(14) The determination of first-order rate constants and of kinetic activation parameters (reported as ± one standard deviation) was accomplished by using the computer program LSTSQ, available from Serena Software, 489 Serena Lane, Bloomington, IN 47401. Molecular mechanics programs adapted from Allinger's MMP1 were also obtained from Serena Software; this version (name: MMPM) with the accompanying graphics routine was run on an IBM-AT microcomputer.

(15) (a) Our reaction of *tert*-butylethylene with anthracene required more vigorous conditions than did the reaction with other alkylethylenes, and the yield was much lower. (b) In another study that documents steric effects in cycloaddition/cycloreversion reactions, dienophiles with increasingly large substituents were shown to undergo dramatically slower forward reactions, yet the rate of the cycloreversion increased only slightly (Vaughan, W. R.; Andersen, K. S. *J. Org. Chem.* **1956**, *21*, 673).

(16) Wiberg, K. B. In *Physical Organic Chemistry*; John Wiley and Sons: New York, 1966; p 376.

**Table I. First-Order Rate Constants of Retro-Diels–Alder Reactions at 250 °C in Diphenyl Ether**

| R | compd | % of reaction used to calculate rate constant | no. of data points | $10^5 k_1$, s$^{-1}$ | rel rate | $\sigma_p$ |
|---|---|---|---|---|---|---|
| H | 1a | 3–83 | 12 | 1.21 | 1.00 | 0.00 |
| Me | 1b | 17–68 | 11 | 1.14 | 0.94 | −0.17 |
| Et | 1c | 2–89 | 10 | 1.09 | 0.90 | −0.15 |
| *i*-Pr | 1d | 18–76 | 10 | 0.97 | 0.80 | −0.15 |
| *t*-Bu | 1e | 8–76 | 8 | 0.88 | 0.73 | −0.20 |
| Ph | 1f | 10–85 | 10 | 146 | 123 | 0.01 |
| SiMe$_3$ | 1g | 11–81 | 10 | 19.6 | 16.2 | −0.07 |
| CO$_2$H | 1h | 19–79 | 11 | 168 | 139 | 0.41 |
| CONH$_2$ | 1i | 5–76 | 9 | 39.8 | 32.9 | 0.36 |
| CO$_2$CH$_3$ | 1j | 10–71 | 9 | 69.0 | 57.0 | 0.39 |
| CN | 1k | 5–82 | 10 | 81.9 | 75.9 | 0.66 |
| COCH$_3$ | 1l | 11–79 | 11 | 217 | 179 | 0.50 |
| CHO | 1m | 22–94 | 11 | 304 | 251 | 0.22 |
| NO$_2$ | 1n | 8–88 | 10 | 20.1 | 16.6 | 0.78 |
| NH$_2$ | 1o | 15–81 | 10 | 100 | 82.9 | −0.66 |
| NHAc | 1p | 5–81 | 9 | 16.7 | 13.8 | −0.01 |
| NMe$_2$ | 1q | *a* | *a* | 3006 | 2480 | −0.83 |
| NMe$_3$$^+$TsO$^-$ | 1r | 20–97 | 11 | 2030 | 1680 | 0.82 |
| OAc | 1s | 5–82 | 10 | 0.40 | 0.30 | 0.31 |
| OH | 1t | 15–81 | 9 | 1.62 | 1.34 | −0.37 |
| OCH$_3$ | 1u | 9–65 | 10 | 2.70 | 2.23 | −0.27 |
| OSiMe$_3$ | 1v | 3–85 | 10 | 2.73 | 2.26 | *b* |

*a* Due to the fast reaction rate at 250 °C, $k_1$ was extrapolated from the temperature dependence.   *b* No known substituent constant.

**Table II. Kinetic Activation Parameters for Some Representative Substituents in the Retro-Diels–Alder Reaction of Anthracene Adducts**

| R | compd | $\Delta H^*$ (kcal/mol) | $\Delta S^*$ (eu) | $T$(avg), °C |
|---|---|---|---|---|
| Me | 1b | 44 ± 1.7 | 2.9 ± 3.2 | 245 |
| *t*-Bu | 1e | 50 ± 2.0 | 14 ± 4.0 | 245 |
| CO$_2$Me | 1j | 38 ± 0.38 | −1.8 ± 0.74 | 245 |
| NMe$_2$ | 1q | 29 ± 0.11 | −11 ± 0.22 | 220 |
| OMe | 1u | 43 ± 3.4 | 2.0 ± 6.5 | 245 |

Second, electron-withdrawing groups on the dienophile fragment make the cycloreversion reaction faster in complete analogy to the forward reaction. Comparing classical electron-donating entries (e.g., 1a–e and 1t–v) to classical electron-withdrawing entries (e.g., 1h–n) makes this point succinctly. The rates are in all cases enthalpically, rather than entropically, controlled, as evidenced by the activation parameters[14] listed in Table II.

Finally (and most interestingly), observed major deviations from a simplistic electron-donating/withdrawing rationale completely invalidate its supremacy as applied to this electrocyclic process. If we use the Hammett $\sigma_p$ constant to characterize electron-donating ($\sigma_p < 0$) or -withdrawing ($\sigma_p > 0$) ability,[17,18] then compounds 1f, 1g, 1m, 1o, 1q, 1s, 1t, and 1u are all significantly (>25 times) faster than can be explained based solely on this parameter.[19] In the most extreme case, the "strongest" electron-donating group, dimethylamino, makes the reaction even faster than does the "strongest" electron-withdrawing group, trimethylammonium! On the basis of its $\sigma_p$ value of −0.83, the dimethylamino group accelerates this reaction

by a factor of 3 × 10$^6$ over that predicted.

A finding this contrary to chemical intuition demands at least one rationalization. We provide five: (1) overlap with the nitrogen p$\pi$ lone pair weakens the adjacent C–C bond;[20] (2) the nitrogen provides a predominant resonance effect that overrides its unfavorable polar effect;[21] (3) the dimethylamino group is the most potent neutral double bond stabilizing group known, resulting in product stabilization that is reflected in the transition structure;[22,23] (4) augmented delocalization in the transition structure as measured by the transition structure valence bond resonance structures to ground state structures ratio;[24] (5) there is movement toward a zwitterionic mechanism.[25] Work aimed at differentiating between these possibilities is not proceeding in these laboratories. However, both

(17) The Hammett $\sigma_p$ constant is only one of several specialized $\sigma$ parameters that could be used to characterize substituents (see ref. 18). However, because it reflects a commonly accepted ranking of the electron-donating/withdrawing ability of these groups, it is an appropriate yardstick for comparison.

(18) (a) Hine, J. In *Structural Effects on Equilibria in Organic Chemistry*; Robert E. Krieger Publishing Company: Huntington, New York, 1981; Chapter 3. (b) Williams, A. In *The Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: Amsterdam, 1984; pp 143–163.

(19) In order to determine relative rates predicted by the Hammett equation, we refered to a line defined by compounds 1a (R = H) and 1r (R = NMe$_3$$^+$); a significant resonance effect is not expected in either of these groups. The equation thusly determined has the form: log ($k_R/k_H$) = 3.93$\sigma_p$.

(20) By direct analogy to the Evan's explanation for oxyanionic acceleration of various electrocyclic processes: (a) Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3319. (b) Steigerwald, M. L.; Goddard, W. A.; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994.

(21) Carpenter predicts that dienophilic substituents possessing a strong resonance effect will increase the rate of both forward and reverse Diels–Alder reactions: Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877. The conjugation effect successfully predicts that Ph, SiMe$_3$, NH$_2$, NMe$_2$, OH, and OMe groups should all be faster than predicted by their $\sigma_p$-based electronic properties if transition structure delocalization is an important factor in this process.

(22) Hine has shown that the dimethylamino group is an extremely potent double bond stabilizing substituent: Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4766. It is interesting to note these results successfully predict that Ph, CHO, NMe$_2$, and OMe should be faster than predicted by their $\sigma_p$-based electronic properties if product stabilization is an important factor in this process. No data was available with which to make predictions for SiMe$_3$, NH$_2$, OAc, and OH groups.

(23) One referee has rightly pointed out that this rationalization may not be consistent with the argument for an early transition structure in this reaction. The issue very quickly becomes quite murky. For example, will the existence of an early transition structure negate the significance of a fading steric effect to the same extent that it will diminish the significance of a developing electronic effect? Because we cannot answer this question simply, we believe that double-bond stabilization must remain a viable rationalization. Following a referee's suggestion, we recognize that high temperature cycloreversions need not retrace the same mechanistic pathway followed in a lower temperature cycloaddition reaction.

(24) Ala Herndon as recently reviewed: Herndon, W. C. *J. Chem. Educ.* **1981**, *58*, 371.

(25) This last possibility is supported by our observed solvent effects on reaction rates. Using pentadecane (nonpolar) and diphenyl ether (more polar) at 250 °C, the relative reaction rates are R = Me, 1.00, 0.99; R = NMe$_2$, 1.00, 5.79.

possibilities (2) and (5) suggest that enamines may not be unreactive in some Diels–Alder reactions of "normal" electron demand; this idea is being pursued.

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## Diels–Alder Reactions of α,β-Unsaturated Acyl–Iron Complexes

*Summary:* Lewis acid catalyzed Diels–Alder reactions between alkyl-substituted 1,3-butadienes and ($\eta^1$-acryloyl)($\eta^5$-cyclopentadienyl)dicarbonyl(II) complexes have been examined and were found to proceed in excellent yields under mild conditions.

*Sir:* Acyl–metal complexes containing the ($\eta^5$-cyclopentadienyl)dicarbonyliron(II) unit and phosphine-substituted analogues have recently emerged as very versatile intermediates for organic synthesis,[1] being easily converted into esters and amides,[1b] rendering α-protons acidic,[1d] and undergoing facile and stereoselective decarbonylation reactions upon photolysis[2] or treatment with rhodium(I) catalysts.[3] In addition, phosphine-substituted analogues of this unit have seen exciting applications in the area of asymmetric induction.[1a] With these recent developments in mind, we were tempted to investigate the behavior of ($\eta^1$-acryloyl)($\eta^5$-cyclopentadienyl)dicarbonyliron(II) complexes 1 (readily available by reaction of α,β-unsaturated acid chlorides with sodium [($\eta^5$-cyclopentadienyl)dicarbonylferrate][4] in Diels–Alder reactions;[5] in this study we report the results of that investigation (Scheme I).

Compound **1b** would not react with cyclopentadiene or isoprene at 0 °C or in refluxing benzene. While the electron-withdrawing ability of the acyl($\eta^5$-cyclo-

Scheme I. **Reaction of α,β-Unsaturated Acyl–Iron Complexes with Dienes and Lewis Acids**
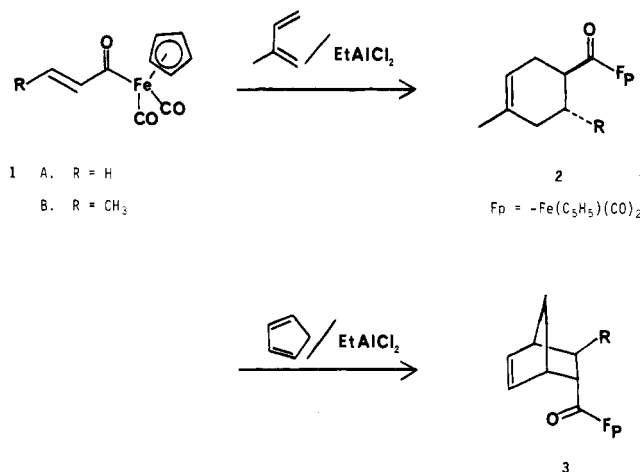


pentadienyl)dicarbonyliron(II) group has not been evaluated quantitatively,[6] chemical shifts of the olefinic carbons in compound **1b** ($C\alpha = 130.3$, $C\beta = 144.9$) vs. those of ethyl crotonate ($C\alpha = 123.3$, $C\beta = 144.0$) suggest that polarization of the double bond by the acyl–metal group is considerably less than that of the carbomethoxy group. Upon addition of 1 equiv of ethylaluminum dichloride or diethylaluminum chloride, the reaction proceeds at 25 °C to give compound **3b** in excellent yields (Table I, entries 1 and 2). Ethylaluminum dichloride is the better of the two catalysts; reaction of **1b** and isoprene with diethylaluminum chloride catalyst proceeds in only 38% yield in refluxing benzene, whereas the same reaction with ethylaluminum dichloride catalyst proceeds in 81% yield at 25 °C. The reacting species in alkylaluminum-catalyzed reactions of compound **1b** is best represented by structure 4; upon addition of ethylaluminum dichloride to compound
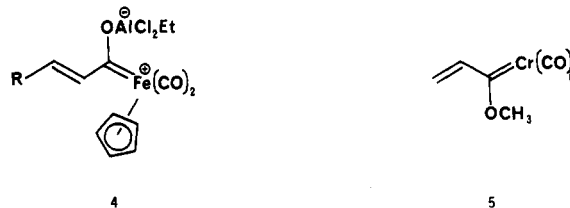


**1b**, a species is produced having a carbon-13 signal at 306 ppm (acyl carbon)[7] which is more consistent with a Fischer–Carbene complex **4b** rather than an acyl–metal complex.[8,9] Analagous vinyl methoxycarbene complexes of chromium(0) (5) have been shown to be excellent dienophiles for Diels–Alder reactions.[10] Other Lewis acid catalysts, boron trifluoride etherate, titanium tetrachloride, and triethylaluminum, were not effective in promoting the desired reaction.

(1) For recent examples, see: (a) Brown, S. L.; Davies, S. G.; Warner, P.; Jones, R. H.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1985,** 1446–1447. (b) Djima, I.; Kwon, H. B. *Chem. Lett.* **1985,** 1327–1330. (c) Liebeskind, L. S.; Walker, M. E.; Helquist, P. *Tetrahedron Lett.* **1985,** 26.

(2) For recent example, see: Bly, R. S.; Silverman, G. S.; Bly, R. K. *Organometallics* **1985,** *4,* 374–383.

(3) Kuhlman, E. H.; Alexander, J. J. *J. Organomet. Chem.* **1979,** *174,* 81–87.

(4) King, R. B.; Bisnette, M. B. *J. Organmet. Chem.* **1964,** *2,* 15–37. Purification via flash chromatography on silicon gel leads to excellent yields of the desired complexes.

(5) **Note added in proof:** (Ferra-β-diketonato)BF$_2$ complexes containing alkenyl substituents undergo Diels–Alder reactions with 1,3-dienes. Lenhert, P. G.; Lukehart, C. M.; Sacksteder, L. *J. Am. Chem. Soc.* **1986,** *108,* 793–800.

(6) Reactivity patterns from ref 1 suggest that the acyl–metal group behaves similarly to a carbomethoxy group.

(7) Carbene complexes of this type (heteroatom substituted) typically have chemical shifts greater than 300 ppm; for a discussion, see: Formacek, V.; Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1972,** *11,* 141–142. In a compound related to **3b** (O–Al replaced by H), the chemical shift of the carbene carbon is 314 ppm. Kuo, G. H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984,** *3,* 806–808.

(8) Infrared spectra of acyl–metal–aluminum chloride complexes suggest the carbene–complex resonance structure. Stimson, R. E.; Shriver, D. F. *Inorg. Chem.* **1980,** *19,* 1141–1145.

(9) For a review on the reactions of transition-metal carbene complexes, see: Doetz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 587–608.

(10) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984,** *106,* 7565–7567. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983,** *105,* 6726–6727.