Aromatization of 1,4-Cyclohexadienes with Tetracyanoethylene: A Case of Varying Mechanisms

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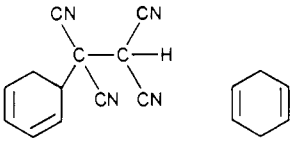
The aromatization of 1,4-cyclohexadiene and four alkyl-substituted 1,4-cyclohexadienes with tetracyanoethylene was examined and found in four of five cases to involve two competing mechanisms. Most of each reaction proceeded by concerted ene addition followed by breakdown of the ene adduct, probably heterolytically. Rate constants for diene reaction were determined in acetonitrile-d_3 and *p*-dioxane-d_8. Adducts were isolated in three cases and rate constants for adduct breakdown determined for the isolated compounds. Where the adduct could be observed but not isolated, a constant was calculated through computer simulation of the rate data. The minor mechanism competing with the ene addition displayed no detectable intermediates and seemed most consistent with electron–proton–electron–proton or electron–proton–hydrogen-atom transfer. Total reaction rate varied by a factor of over 4×10^5, yet with one exception, the ratio of the two pathways varied very little. One possible explanation for this, the presence of a common rate-determining step preceding any hydrogen transfer (such as SET) was ruled out by the finding of a large primary isotope effect for hexadeuterio-1,4-cyclohexadiene disappearance ($k_H/k_D = 5.2$). With one diene, 3,3-dimethyl-1,4-cyclohexadiene, the otherwise minor mechanism became the sole one, as the adduct formed was clearly not a concerted ene adduct. However, in this case aromatization also required a 1,2 methyl shift, and the fact that quantitative collapse to an adduct, without rearrangement, occurred instead ruled out a simple cation intermediate from hydride transfer. A reversible electron transfer therefore seems the likeliest first step for the minor mechanism.

Tetracyanoethylene (TCNE) reacts with 1,4-cyclohexadienes (1,4-CHD's) to give tetracyanoethane and the corresponding arene.[1,2] Although this reaction has not been applied with anything approaching the frequency of similar aromatization reactions using quinones (e.g. *o*-chloranil or 2,3-dichloro-5,6-dicyanobenzoquinone[3]) yet, it is often very mild, has synthetic utility,[4] and perhaps might see more use if it were better understood.

Nishiguchi et al. proposed a stepwise mechanism involving hydride abstraction or electron–proton–electron transfer to give a cyclohexadienyl cation for the TCNE reaction.[5] A little earlier, Haselbach and Rossi, during an investigation directed largely at another matter, had isolated a reactive intermediate, 1, from the reaction of



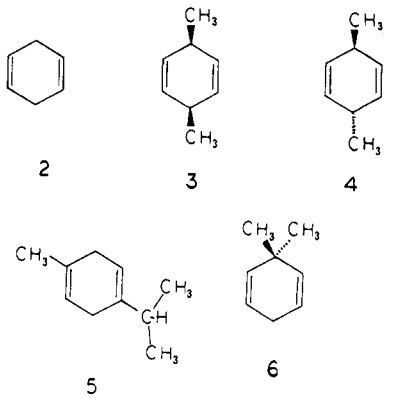
1 2

TCNE and 1,4-CHD (**2**).[6] They ascribed its formation, apparently in very low yield, to an ene reaction, but they did not determine how much of a role it had in the overall aromatization process. They did tentatively suggest a base-catalyzed E_2 reaction for the breakdown of the intermediate to benzene.

One of us had already noted that TCNE was a very good enophile, particularly toward substituted 1,3-cyclohexadienes,[7] and therefore decided to look with a more direct focus on the role of the ene reaction in the TCNE-mediated aromatization of 1,4-CHD's. In a preliminary report,[8] the aromatization was found to proceed by initial concerted ene reaction followed by breakdown to an intermediate such as the posited cyclohexadienyl cation. We now are presenting the results of an examination of the reaction of TCNE with a set of substituted 1,4-CHD's as well as a more complete analysis of the data for the unsubstituted diene.

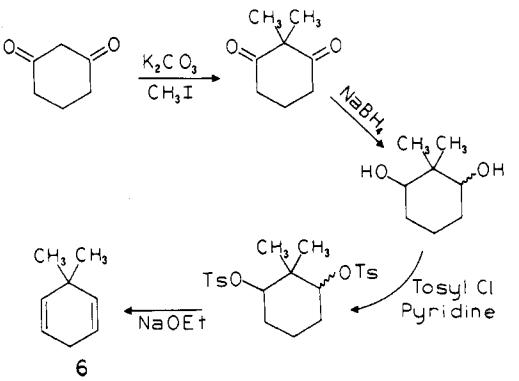
The compounds examined are shown in Chart I. All are known in the literature but only 1,4-cyclohexadiene and

Chart I



2 3 4 5 6

Scheme I



6

1-isopropyl-4-methyl-1,4-cyclohexadiene (γ-terpinene, **5**) are commercially available, with the latter not in very pure

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(1) Longone, D. T.; Smith, G. L. *Tetrahedron Lett.* **1962**, 205.
(2) Longone, D. T.; Boettcher, F.-P. *J. Am. Chem. Soc.* **1963**, *85*, 3436.
(3) Jackman, L. M. *Adv. Org. Chem.* **1960**, *2*, 239.
(4) For example: Berson, J. A.; Willcott, M. R. III. *J. Am. Chem. Soc.* **1965**, *87*, 2751.
(5) Nishiguchi, T.; Ohki, A.; Sakakibara, H.; Fukuzumi, F. *J. Org. Chem.* **1978**, *43*, 2803.
(6) Haselbach, E.; Rossi, M. *Helv. Chim. Acta* **1976**, *59*, 2635.
(7) Jacobson, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 146. Jacobson, B. M.; Feldstein, A. C.; Smallwood, J. I. *J. Org. Chem.* **1977**, *42*, 2849.
(8) Jacobson, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 886.

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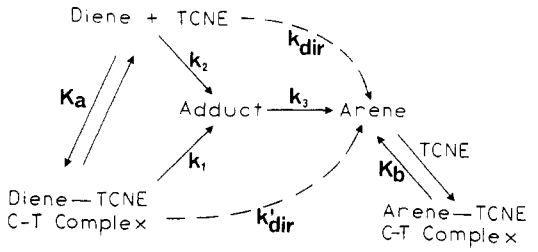
Scheme II



form. The syntheses of **3** and **4** were accomplished by using the route of Stoos and Roĉek.[9] We prepared **6** by a new route (Scheme I) because the literature route[9] gives a rather low yield and its product is also difficult to purify.

Because we were most interested in whether any ene or other adducts formed as intermediates, we decided to use ^{1}H NMR as our main tool to follow the reactions. Since TCNE has no protons to be integrated in the NMR spectrum, we could not use a large excess of diene without reducing the accuracy of the rate measurements, i.e., we could not run the reaction under pseudo-first-order conditions. We also anticipated that while any intermediate would probably form in a second-order process, its further reaction might well differ in kinetic behavior (we had found that **1** decayed in a first-order manner[8]). Maximizing the concentration of the intermediate for ease of observation thus required a high initial concentration of both reactants, with certain attendant problems and benefits discussed below.

The dienes and, more importantly, the aromatic products, also form charge-transfer (CT) complexes with TCNE. With comparable diene, TCNE, and sometimes arene concentrations present, we initially expected that complex formation would affect the concentration of free TCNE and free diene in a time-dependent manner, complicating the kinetics.

The change created by a charge-transfer complex intermediate in the kinetic equation for an addition reaction was discussed by Andrews and Keefer for maleic anhydride cycloadditions,[10] extended to TCNE reactions by Rappoport,[11] and succinctly summarized by Haselbach,[6] but in each case only for pseudo-first-order reaction conditions where complexation of the product could be ignored. After adding a direct route to product (the dashed lines in Scheme II), allowing for complexation of the product by TCNE and considering only processes first order in the latter, their equations for disappearance of diene become the kinetically indistinguishable equations (1 and 2), de-

$$k_{obs} = \frac{k_1K_a + k_{dir}K_a}{(1 + K_a[A_f])(1 + K_a[D_f] + K_b[P_f])} \quad (1)$$

$$k_{obs} = \frac{k_2 + k_{dir}}{(1 + K_a[A_f])(1 + K_a[D_f] + K_b[P_f])} \quad (2)$$

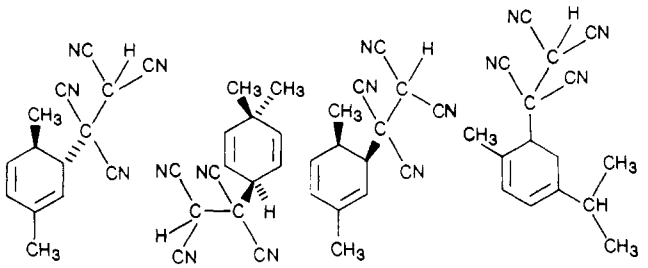
pending on whether reaction proceeds via the CT complex. (A_f = uncomplexed TCNE, D_f = uncomplexed diene, and P_f = uncomplexed arene product concentrations, respectively.) If complexed and uncomplexed dienes both react, k_{obs} is simply the sum of the two equations.

Second-order plots using total diene and TCNE concentrations therefore should not give straight lines. However, further analysis (see calculations in the Experimental Section) and a few simple experiments convinced us that the curvature would be too small to see or to affect our conclusions.

Results

All the dienes reacted with TCNE in acetonitrile-d_3 or dioxane-d_8[12] in a two-stage process to give first a 1:1 adduct and then the arene plus 1,1,2,2-tetracyanoethane. In three cases, with **2**, **3**, and **5**, we have strong evidence that each adduct was formed in a concerted ene reaction. With **6**, adduct clearly formed by a nonconcerted route, and only with **6** did the reaction proceed entirely via the observed intermediate. There does appear to be a trace of a second adduct with **6**, but it could not be isolated and may result from an impurity in or isomerization of the diene.

The intermediates **7** and **8**, from **3** and **6**, respectively, were isolated as **1** had been earlier.[6,8] By NMR, **7** clearly had the conjugated structure shown, with one methyl group a finely spaced triplet at δ 2.13 (1,3-allylic coupling) and the other still a doublet at δ 1.37, close to the position of the methyl signal in the original diene.



7 **8** **9** **10**

On the other hand, **8** showed both methyls shifted only by ~0.1 ppm from their original position, and although now nonequivalent, both were still singlets. The vinyl hydrogens in **8** show a complex but fairly symmetric pattern, much more symmetric than the pattern from those in **1**. However, it is the UV spectrum that makes the nonconjugated structure obvious, with a λ_{max} at 205 nm and only end absorption at longer wavelengths.

We could not isolate the intermediates detected in the reactions of **4** and **5**. They are drawn here with what we believe are their structures (**9** and **10**). The weak, short-lived signals seen for **9** during the reaction of **4** and TCNE were at almost exactly the same chemical shifts as those seen for the vinyl hydrogen and allylic methyl signals of **7**. We are thus confident it too is a concerted ene adduct. With **5** and TCNE, the even shorter lived but stronger signals included an "AB" pair of doublets at δ 5.8 and 6.2 (J = 8 Hz), consistent with the conjugated structure **10**, but not with any other reasonable structure.

The decompositions of both **1** and **7**, to give benzene and *p*-xylene, respectively, were simple, quantitative, first-order processes with a substantial dependence on solvent polarity. The intermediates **9** and **10**, though they could not be isolated, reacted in similar fashion, respectively yielding *p*-xylene and *p*-cymene quantitatively. The intermediate **8** behaved more complexly. During the original reaction of TCNE and **6**, it decomposed very slowly but apparently as the other intermediates did. However, after most of **6** was gone, the adduct decomposition rate suddenly doubled. When isolated and placed in the pure reaction solvent, **8** decomposed in a first-order reaction but at the second, faster rate. Further, from the mass balance calculated from

(9) Stoos, F.; Roĉek, J. *J. Am. Chem. Soc.* **1972**, *94*, 2719.
(10) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 6284, and earlier papers noted therein.
(11) Rappoport, Z.; Horowitz, A. *J. Chem. Soc.* **1964**, 1348.
(12) In our earlier work[8] we had used tetrahydrofuran rather than dioxane but found the results less reproducible, possibly because of evaporation of the more volatile THF during sample preparation.

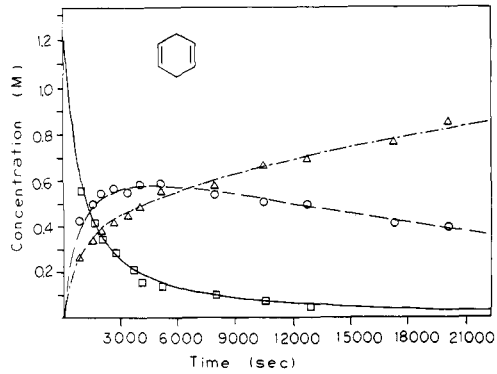


Figure 1. Experimental and calculated values for the concentrations of 1,4-cyclohexadiene (□, exptl; — calcd), **1** (○, exptl; - - -, calcd), and benzene (△, exptl; – – –, calcd). TCNE is in small excess, CD_3CN solvent. Data for an additional 30 000 s not shown.

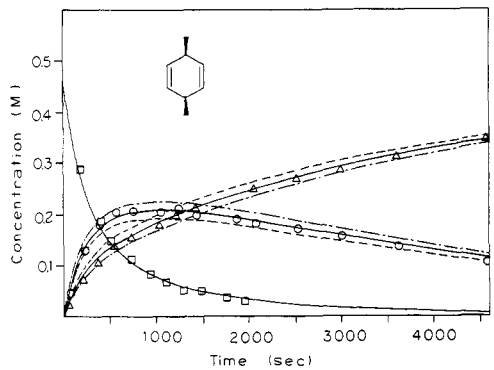


Figure 2. Experimental and calculated values for the concentrations of *cis*-3,6-dimethyl-1,4-cyclohexadiene (□, exptl; —, calcd), **7** (○, exptl; —, calcd with $F = 0.63$; - - -, calcd with $F = 0.58$; – – –, calcd with $F = 0.68$), and *p*-xylene (△, exptl; —, calcd with $F = 0.63$; - - -, calcd with $F = 0.58$; – – –, calcd with $F = 0.68$). TCNE is in small excess, CD_3CN solvent. Data for an additional 4000 s not shown.

NMR integrals, the yield of *o*-xylene was far from quantitative during the faster process but appeared to be nearly so in the original slower one. All the directly observed rate constants for the reactions are given in Table I.

As we could not isolate **9** and **10**, we could only roughly estimate the rate constants k_3 for their decomposition as it accompanied the reactions of their parent dienes. With **9**, the estimation was made difficult because a significant amount of adduct continued to form through most of the period that we could measure its low concentration at all. The concentration of **10** was transiently much higher but again fell quite low before the diene was consumed, and in addition, the reaction was simply too fast to allow us to get very accurate data. We therefore resorted to an indirect calculation of the rate constants for these two cases.

There does not appear to be an analytical solution in the literature for the differential equations representing the changes in concentration for the sequence of a second-order reaction A + B → C followed by a first-order step C → D. Therefore, using the experimental k_{obs} for diene disappearance and an estimate for k_3, we integrated numerically. We then plotted calculated concentration values along with the measured diene, adduct, and arene ones, planning to vary k_3 until we got the lines to match the experimental data. To validate our procedure, we first used it on **2**, **3**, and **6** to be sure it reproduced the data where both rate constants were known. We immediately saw a large discrepancy between the calculated and observed adduct and arene concentrations for **2** and **3** but

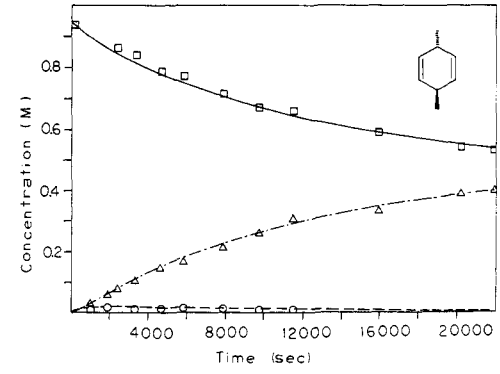


Figure 3. Experimental and calculated values for the concentrations of *trans*-3,6-dimethyl-1,4-cyclohexadiene (□, exptl; —, calcd), **9** (○, exptl; - - -, calcd), and *p*-xylene, (△, exptl; – – –, calcd). Diene is in 2-fold excess over TCNE, CD_3CN solvent.

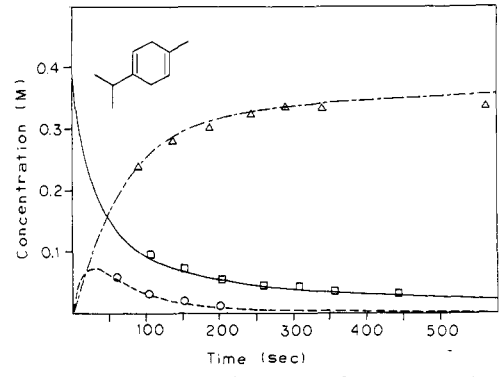


Figure 4. Experimental and calculated values for the concentrations of γ-terpinene (□, exptl; —, calcd), **10** (○, exptl; - - -, calcd), and *p*-cymene, (△, exptl; – – –, calcd). TCNE is in small excess, CD_3CN solvent.

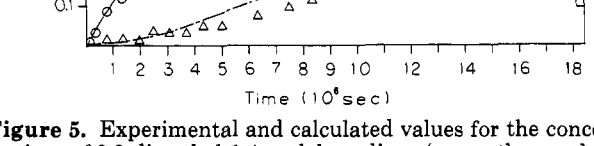


Figure 5. Experimental and calculated values for the concentrations of 3,3-dimethyl-1,4-cyclohexadiene (□, exptl; —, calcd), **8** (○, exptl; - - -, calcd), and *o*-xylene, (△, exptl; – – –, calcd). TCNE is in small excess, CD_3CN solvent.

not for **6**. We then modified the calculation, adding a fractional multiplier F for k_{obs} so that only a portion of the diene formed the adduct and the rest was immediately converted to arene. We then varied this fraction until the calculated and observed concentrations had their best match.

Figures 1 and 2 show the best matches found for **2** and **3**. The curves were quite sensitive to the F parameter and Figure 2 shows how clearly the calculated curves varied with small changes in F. We then proceeded to the calculations for **4** and **5**, now with two variables. Unfortunately, it was possible to fit the limited data we had fairly well over a fair range of F and k_3 values, for **4** because the

Table I. Rate Constants for Diene and Adduct Reactions at 35 °C

diene	solvent	$10^6 k_{obs}$,[a,b] M^{-1} s^{-1}	r[c]	$10^6 k_3$,[b,d] s^{-1}	r[c]	F[e]
2	CD_3CN	1030 ± 50	0.995	31 ± 1.6	0.997	0.60
2	CH_3CN	932 ± 1[f]	0.999	*g*		*g*
2-d_6	CH_3CN	180 ± 5[f]	0.998	*g*		*g*
2	THF	88 ± 9	0.980	7 ± 1	0.985	0.75
3	CD_3CN	7080 ± 170	0.996	235 ± 8	0.997	0.63
3	dioxane-d_8	1650 ± 80	0.994	35 ± 1.3	0.996	0.78
4	CD_3CN	94 ± 2	0.997	1600 ± 800[h]		0.65 ± 0.35[h]
4	dioxane-d_8	18 ± 0.8	0.996	50 ± 30[h]		0.70 ± 0.30[h]
5	CD_3CN	85000 ± 5000	0.994	30000 ± 10000[h]		0.68 ± 0.32[h]
5	dioxane-d_8	8300 ± 700	0.992	*i*		*i*
6	CD_3CN	0.174 ± 0.003	0.996	0.13 ± 0.01[j]	0.995	1.0
6	CD_3CN[k]	2.35 ± 0.1	0.994	3.6 ± 0.2[l]	0.992	1.0
6	dioxane-d_8[k]	0.38 ± 0.02[m]	0.994	0.3 ± 0.1[h]		1.0

[a] Total rate of disappearance of diene as determined byu NMR. [b] The ± value is the average of the standard deviations in the least-squares calculations. [c] Average of the correlation coefficients in the least-squares calculations. [d] Rate of adduct disappearance by NMR. [e] Fraction of diene converted to adduct according to curve-fitting calculation. [f] As determined by HPLC. [g] No value obtainable because of experimental method used. [h] Determined from curve-fitting calculation. The F and k_3 values are not independent. The ± value is the range over which the curve can be fitted while both values are allowed to vary. [i] Adduct concentration too low for any meaningful calculations. [j] Curve-fitting rate is 60% of this value before the rate break. [k] At 65 °C. [l] Curve-fitting rate is 40% of this before the rate break. [m] Low mass balance: TCNE decomposing.

concentrations of adduct were so low that the curve was very flat near its maximum and for **5** because the reaction was so fast that we could not get a measurement until after the maximum concentration of adduct had already been reached. The values given in Table I are the most nearly "central" pair (Figures 3 and 4 show curves for these).[13] The calculation for **6** did not need an F parameter (i.e. F = 1.0) but showed the clear break in the rate of decomposition of **8** (Figure 5).

Discussion

The adducts formed from **2–5** are clearly the result of concerted ene addition. Their structures rule out hydride abstraction, or any other path proceeding via a cyclohexadienyl cation, as a route to adduct formation. That cation should be recognized as simply the σ-protonated arene. Quite a number of molecular orbital calculations have been performed on protonated benzene[14] and protonated toluene,[14d,15] and it has been found consistently that in benzene it is the carbon para to the site of protonation that bears the greatest charge density. In para-protonated toluene the methyl group enhances this effect. We would not expect there to be much preference for keeping a conjugated system upon ion pair collapse, since conjugation provides very little extra stability in the cyclohexadiene system.[16] Thus, the position that is expected to have the greatest charge density in any cations from **2**, **3**, and **4** should be the likeliest site of attachment for the tetracyanoethyl group upon collapse of an ion pair. In each case this is *not* the position of attachment found (nor the one predicted for an ene reaction). Considerations of steric hindrance would not seem to alter this expectation, as all the positions at which collapse is possible in **3**, **4**, and **5** are similarly hindered: either tertiary or secondary with a β branch. A mixture of isomers seems almost certain to be the result if ion pairs from hydride abstraction were to form any adducts. We have no evidence for formation of more than one adduct except for a trace of a second one with **8**. However, in this case the structure of the major adduct is still inconsistent with the cation route's prediction, for a different reason discussed below.

The rates in Table I show tremendous variation for both steps of the aromatization process. The fastest diene reacts over 400 000 times faster than the slowest. The range of rates for disappearance of the adducts is nearly as large. Under Scheme II we would ascribe the first of these large ranges to stereoelectronic effects.

The ene reaction has strong geometrical constraints: the hydrogen being abstracted must be coplanar with the π orbital to which the enophile will bond.[17] In a six-membered ring donor, this means the enophile must approach from above or below the ring. 1,4-CHD rings are thought to be essentially planar.[18] Thus, although not fully axial, the methyls in **4** and **6** will lie above and below the ring plane and make the approach by the relatively bulky TCNE more difficult. Since the enophile must also form a bond vicinally to these methyls, the steric effect is magnified. In the case of **6** where there is buttressing of the methyl groups, this apparently causes the ene reaction to be supplanted altogether.

On the other hand, it is known that the ene reaction is enhanced substantially when the abstractable hydrogen is on a more substituted ring carbon and the substitution does not interfere with the approach of the enophile.[19] As a result, **3**, where one side of the ring remains unhindered, is much more reactive than **2**. Where the extra substituent does interfere, as in **4**, the two effects largely cancel. We assume that the alkyl groups in **5** contribute to a similar weakening of the bond to the departing hydrogen although only one group can be positioned allylically at the transition state. The rate increase seems overly large, but there is probably also less steric hindrance in **5** because the substituents lie essentially in the mean plane of the ring.

There remains the matter of the "direct" aromatization route that is the minor pathway competing with the ene reaction for **2** and **3–5** and is assumedly then the sole

(13) Although the full ranges of k_3 and F that can produce reasonable looking curves are given as the uncertainties, the true values are unlikely to be near the extremes because the values are not independent. If both are placed near their limits the calculated curve is clearly outside the experimental results.

(14) (a) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240. (b) Schoeller, W. W.; Schenck, G. E. *Tetrahedron* **1973**, *29*, 425. (c) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598. (d) Ermler, W. C.; Mulliken, R. S. *Ibid.* **1978**, *100*, 1647. (e) Binning, R. C., Jr.; Sando, K. M. *Ibid.* **1980**, *102*, 2948.

(15) Hehre, W. J.; McIver, R. T., Jr.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7162.

(16) Turner, R. B.; Mellon, B. J.; Tichy, M.; Doering, W. v. E.; Roth, W. R.; Schröder, G. *J. Am. Chem. Soc.* **1973**, *95*, 8605.

(17) For a thorough review of the ene reaction, see: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

(18) Rabideau, P. W.; Lipkowitz, K. B.; Nachbar, R. B., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3119.

(19) Jacobson, B. M.; Arvanitis, G. M.; Eliasen, C. A.; Mitelman, R. *J. Org. Chem.* **1985**, *50*, 194.

pathway with **6**. There is no concerted route possible for the formation of **8**, but if a hydride ion were to be abstracted from **6**, it ought to rearrange before it could combine with the tetracyanoethyl anion to form an adduct. The barrier to 1,2-migration in the cation should be quite small, probably no more than the 4 to 6 kcal/mol seen for other simple methyl migrations.[20] Although there are few values available for the barrier to collapse of a tight ion pair, those that are, are much larger.[21] Thus, neither of our expected routes was observed with **6**.

What also seemed remarkable, given the immense rate variation, was that except for **6**, F did not vary much from diene to diene (although it varied slightly with solvent); i.e. the two mechanisms "track" each other closely with changes in diene structure. Also very unusual is the solvent polarity dependence of the rate, much larger than typical for ene reactions.[17,22] These items, along with the need for some noncation intermediate in the formation of **8** and the possibly anomalous reactivity of **5**, led us to consider an alternate pathway for the overall reaction.

A simple explanation for the tracking of the reactions would be that there is no fully separate second mechanism at all but only a partitioning: a single intermediate forming in the rate-determining step and then diverging steps leading either to the ene adduct or directly to arene. If the rates of these later product determining steps were only slightly (or very similarly) structure-dependent, near constancy of F would result. We hypothesized that the rate-limiting step was formation of a radical-cation, radical-anion pair by single electron transfer (SET), followed by concerted ene reaction of the radical ions in competition with proton abstraction. It was a particularly attractive idea because it has been shown that facile Diels–Alder reactions can occur via radical cations.[23]

It should be noted in passing that because of CT complex formation, any electron transfer taking place will be "inner sphere". Calculations from Marcus theory that would predict unacceptably low rates of reaction for these quite endergonic electron transfers[24] are therefore not applicable. Kochi et al.[25] have noted this in reactions of TCNE with alkyltins and further ascribe the large steric effects they saw as symptomatic of the intervening role of the CT complex before SET.

The unusually large solvent dependence of our ene reactions was one item in support of SET. Further, while the absence of methyl migration ruled out the cyclohexadienyl cation as an intermediate in the formation of **8**, a 1,2-migration in a radical should be much slower than collapse of a radical pair. SET followed by proton abstraction and collapse of the resulting radical pair would seem to be the simplest acceptable path to **8**. Although lesser steric hindrance may be the sole cause for the high rate of reaction of **5**, it is also consistent with SET, since **5** is the only one of our dienes with additional alkyl substitution directly on the double bonds, where it would lower the ionization energy.

There is a straightforward if laborious test for *rate-determining* SET here. Most concerted ene reactions of allylically deuteriated alkenes have shown a substantial primary isotope effect.[17] Rate-determining SET should

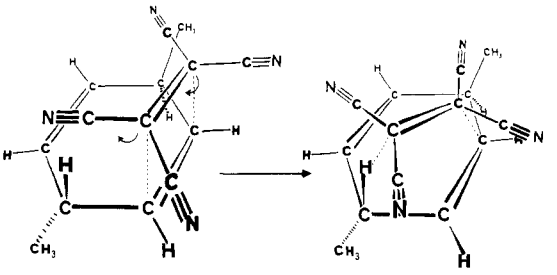
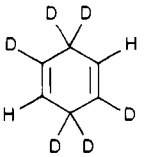


Figure 6. Projection from models of motion from CT complex to ene adduct formation geometry for **4** and TCNE.

show only a small secondary isotope effect. A hexadeuteriated form of **2** (**2**-d_6) was prepared by a slight



2-d_6

modification of a literature scheme.[26] We then determined the rate constant for disappearance of **2**-d_6 reacting with TCNE and found a k_H/k_D of 5.2.[27]

Rate-limiting SET is thus ruled out, although *reversible* electron transfer is not. As this seems the only reasonable path for the reaction of **6**, and we are reluctant to invoke yet a third mechanism unnecessarily for the minor reaction path of the other dienes, we still favor such transfer for the latter, and hope yet to test this in another way. But without rate-limiting SET, how are the near constancy of F and the solvent-rate dependence to be explained? If there is a mandatory charge-transfer complex on the reaction path we believe this can be done.

Barring SET, the unusually large solvent dependence of our ene reaction is consistent with the need for a CT complex, as that would be the only polar point on the ene reaction path.[28] Kiselev and Miller devised a scheme to determine the role of the complex in a cycloaddition reaction of TCNE,[29] but the necessary condition for application of their method, that $-\Delta H°$ for the complex be greater than $\Delta H^{\ddagger}_{k1}$, is almost certainly not met here for any of the dienes. Yet there is a piece of evidence, again in the reactivity of **6**, that points to a requirement for, or at least a lower energy pathway with, a CT complex.

The methyl groups in **6** should contribute significantly to any rate change only in a negative way, through steric hindrance. First, assume there is no electron transfer, just an ene reaction competing (unsuccessfully) with some kind of direct abstraction.[30] While it is easy to see why **6** is

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(25) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.

(26) (a) Bailey, D. S.; Lambert, J. B. *J. Org. Chem.* **1973**, *38*, 134. (b) Karel, K. J.; Brookhart, M.; Aumann, R. *J. Am. Chem. Soc.* **1981**, *103*, 2695.
(27) We thank a referee of an earlier version of this paper for insisting that we finally carry out this repeatedly delayed experiment.
(28) A referee has argued that solvent effects may be more complex than just the imposition of simple polarity differences, based on the apparent lack of correlation between solvent polarity and rate in the work of Kiselev and Miller.[29] But in that work, those solvents showing anomolously low rates were precisely the ones that complex more strongly with TCNE and thereby effectively lower its activity. The lowest rates are with the aromatic solvents, and the other ones obviously "out of place" such as acetonitrile also bind TCNE well. It is true we have only two solvents in this work, but they have almost the same equilibrium constants for complexation with TCNE[42] so that the comparison using their polarity difference should be a valid one.
(29) Kiselev, V. D.; Miller, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 4037.
(30) We note that molecule-induced homolysis from the CT complex rather than separate electron and proton transfer would also fit our results, but we are unaware of any precedent for such a process with TCNE.

much slower to react than **2** along the ene pathway, it is not easy to see why it should also be some 2000 times less reactive than **2** along the direct pathway (relative rate = $(F_6 - F_2) \times (k_{obs2}/k_{obs6})$) unless that too has a strong steric requirement. The simplest way to satisfy this observation is by having both reactions go through the same sterically hindered intermediate, or through ones similarly difficult to achieve. Mandatory charge-transfer complex formation would meet this requirement. (Mandatory but now reversible electron transfer for both reactions would also meet the requirement, for such transfer surely proceeds only, or at least much faster, from the complex.) No other processes likely to be in common to both paths come to mind.

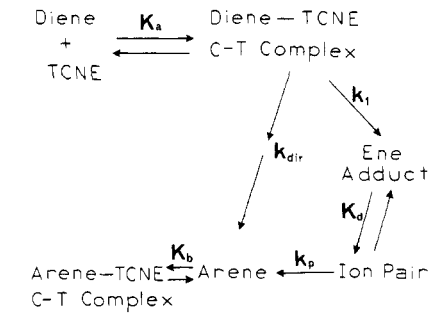
The geometry of a CT complex with an alkene is usually thought of as placing the donor and alkene in a stacked arrangement with parallel π orbitals.[31,32] This is very nearly the geometry needed for the ene reaction. The TCNE would only have to be rotated slightly to be over the transferring hydrogen (Figure 6) to give the ene reaction geometry *and virtually the same motion would be needed for the TCNE to reach the same hydrogen if simple proton abstraction takes place instead.* Steric hindrance should have already played most of its role in setting the equilibrium constant for complex formation. It should become irrelevant to further reaction unless it is so extreme that it magnifies the barrier to the remaining very similar motions to where they are again energetically differentiated, as in **6** with its buttressing methyls.

The mechanism for the breakdown of the various adducts to arene is not entirely clear. We had proposed[8] that for **1** it started with heterolytic fission, based on its first-order disappearance and the strong solvent dependence for the rate. At present, for the other adducts we have only the comparison of the rates in acetonitrile and dioxane, but note that the change in rate is even larger for **7** and **9** than it was for **1**, assuming that tetrahydrofuran and dioxane are essentially identical in polarity.[34]

During the determination of the isotope effect for **2** vs **2**-d_6, experimental difficulties prevented us from obtaining an accurate value of the isotope effect on either F or the decomposition of the ene adduct. However, with the undeuteriated diene there was very little lag between diene disappearance and benzene appearance since in these much more dilute solutions the adduct was formed more slowly. There was a pronounced lag with the deuteriated diene, indicating that adduct was now building up and implying a large isotope effect in its decomposition. Adduct breakdown must be multistepped; certainly no concerted mechanism suggests itself. The lag implies that the initial fission must be reversible, allowing proton transfer again to be in the rate-determining step. We hope to explore this matter further as well as to prepare at least some of the other deuteriated dienes and adducts.

At this stage, our picture of these reactions (Scheme III) is thus (1) charge-transfer complex formation, (2a) ene reaction to give adduct or (2b) reversible electron transfer

Scheme III[a]



[a] $k_{obs} = K_a(k_1 + k_{dir})$. $k_3 = K_d k_p$.

to give radical ion pairs, and (3a) breakdown of the ene adduct or (3b) proton abstraction from the radical cation by the radical anion leading to the direct aromatization by subsequent hydrogen atom (or $e^- - H^+$) abstraction. With **6**, the ene reaction is sterically suppressed, and rapid direct aromatization is prevented by the requirement for methyl migration before a hydrogen atom can be abstracted, so collapse to adduct **8** follows the first proton transfer.

We have been unable to determine a rate constant for decomposition of **10** in dioxane, and for **8** the rate of both formation and decay in dioxane is too low to measure reliably at 35 °C (half-life of over a year). At 65 °C we see a sixfold rate decrease on going from acetonitrile to dioxane for the decay of **8** but the picture is complicated by poor mass balance during the reaction as well as noticeable destruction of TCNE if adduct formation is run at this temperature. There is also the matter of the sudden change in the rate of decomposition of **8** during the reaction of **6**. We therefore feel the mechanism of conversion of **8** to *o*-xylene remains an open question.

There are other unanswered questions for these reactions. The structure of **8** lets us make the otherwise very difficult distinction between e^-–H^+–e^- and hydride transfer[36] for **6**, but we have no proof that the other dienes use the same pathway for their minor route. Secondly, during adduct breakdown, it is not clear why the rate of (heterolytic?) fission should vary so hugely among all the adducts (range $> 2 \times 10^5$).

More complex substitution on the diene may also play roles other than the ones we have already explored. In this regard, Heesing and Müllers have shown that when 1,2-dihydronaphthalene is aromatized by TCNE, a small amount of an adduct is formed and that adduct has the wrong regiochemistry to be an ene product.[37] We have found, in some results still too preliminary to discuss here, that 1,4-dihydronaphthalenes by contrast show a multiplicity of paths in their reactions with TCNE, and they may shed further light on substituent roles.

Experimental Section

Materials. TCNE (Eastman) was sublimed before use. Acetonitrile-d_3 and *p*-dioxane-d_8 (both Aldrich) were used as received. *m*-Dinitrobenzene (Fisher) used as an internal integration standard in NMR was used as received after recrystallization of a sample from ethanol showed no change in mp or NMR. γ-Terpinene (Pfalz & Bauer) was first distilled and then purified further by preparative VPC on a $^3/_8$ in. × 14 ft 15%

(31) (a) *Chemistry of the Cyano Group*; *Rappoport*, Z., Ed.; John Wiley: New York, 1970; pp 639–669. (b) Herbstein, F. H. *Persp. Struct. Chem.* **1971**, *4*, 169. (c) Prout, C. K.; Kamenar, B. *Mol. Complexes* **1973**, *1*, 151.

(32) It may be argued that the arrangement in Figure 6 is a repulsive π2s + π2s one, but it appears that in weak CT complexes the dominant attractive energy interaction is from polarizability (dispersion) effects and a parallel arrangement of the π orbitals maximizes this.[33]

(33) (a) LeFevre, R. J. W.; Radford, D. V.; Stiles, P. J. *J. Chem. Soc. B* **1968**, 1297. (b) Lathan, W. A.; Pack, G. R.; Morokuma, K. *J. Am. Chem. Soc.* **1975**, *97*, 6624.

(34) Dioxane and tetrahydrofuran have identical B and nearly identical A parameters on Swain's solvent polarity scales.[35]

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(36) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

(37) Heesing, A.; Mullers, W. *Chem. Ber.* **1980**, *113*, 24.

Carbowax 20M (60/80-mesh Chromosorb P) column in an Aerograph A-90 chromatograph at 145 °C. 1,4-Cyclohexadiene (Aldrich) was freed of a small amount of benzene by preparative VPC on the same column but at 60 °C. Both *cis*- and *trans*-3,6-dimethyl-1,4-cyclohexadiene were prepared by the method of Stoos and Roček and purified by preparative VPC on a $^3/_8$ in. × 14 ft 15% SE-30 (60/80-mesh Chromosorb P) column at 125 °C. All dienes were sealed in glass ampules until used.

2,2-Dimethyl-1,3-cyclohexanedione. To a three-necked flask equipped with a mechanical stirrer were added 14.5 g of 1,3-cyclohexanedione (Aldrich) in 100 mL of acetone, 35 g of K_2CO_3, and 41 g of CH_3I. The mixture was stirred and refluxed gently for 13 h. After cooling, 100 mL of $CHCl_3$ was added and the mixture filtered. Removal of the solvent under reduced pressure and distillation through a 0.7-m column of glass helices (at 7 mmHg) gave 9.8 g (54%) of the product at 94–96 °C plus 4 g of 3-methoxy-2-cyclohexen-1-one (102–105 °C). The product crystallized upon cooling and was used in the next step without further purification, although VPC indicated some 7% of the higher boiling compound as an impurity.

***cis*- and *trans*-2,2-Dimethyl-1,3-cyclohexanediol.** The product from the previous reaction was stirred with dilute NaOH and excess $NaBH_4$ at 50 °C until no ketone was left (tested with 2,4-dinitrophenylhydrazine). The mixture was cooled and 20 g of K_2CO_3 was added. Both oil and crystals separated. The crystals were collected, washed with ice–water, and dried to give 10 g of the cis diol contaminated by some carbonate. Extraction of this solid with hot acetone and evaporation of the solvent gave 7.4 g (73%) of diol, mp 105–109 °C. The oil, which was slightly soluble in water but not miscible with ether or CH_2Cl_2, was returned to the aqueous reaction mixture and the combination extracted with CH_2Cl_2. Evaporation of the solvent gave 1.5 g (15%) of the impure trans diol, mp 78–90 °C.

***cis*-2,2-Dimethyl-1,3-cyclohexanediol Bis(*p*-toluenesulfonate).** The cis diol (8.5 g) was dissolved in 80 mL of dry pyridine and cooled in ice, and 28 g of purified[38] *p*-toluenesulfonyl chloride was added. After 36 h at room temperature the mixture was poured onto 200 g of ice in 300 mL water and stirred to bring about solidification. The crystals were collected, briefly air-dried, and then dried in a vacuum dessicator over H_2SO_4 to give 25.1 g (93%) of the product.

3,3-Dimethyl-1,4-cyclohexadiene. A solution of sodium ethoxide was prepared from 7.5 g of Na, and 150 mL of ethanol and 12 g of the bis(tosylate) was added to the warm solution. The mixture was stirred and refluxed 24 h, cooled, poured onto 400 mL of ice and water, and extracted with three 50-mL portions of pentane. The combined pentane layers were dried with anhydrous Na_2SO_4 and filtered, and most of the pentane was removed by careful distillation through a 10-cm column of helices. The residue (10 mL) was then distilled through a short Vigreux column to give 2.1 g (76%) of the diene, bp 110–113 °C. Analytical VPC showed it was 91% pure with only pentane and decane (used as a chaser in the distillation) as measurable impurities. Preparative VPC at 95 °C on the Carbowax column used earlier to purify the γ-terpinene afforded 1.6 g of very pure diene.

***trans*-6-(1,1,2,2-Tetracyanoethyl)-2,5-dimethyl-1,3-cyclohexadiene (7).** A 5-mL Schlenk tube equipped with a micro stirring bar was purged with N_2 and charged with 0.295 g of **3**, 1.7 mL of dioxane-d_8, and 0.2 g of TCNE. The mixture was stirred and periodically sampled by syringe, with examination by NMR of the sample which was then returned to the reaction mixture. Most of the TCNE had dissolved after 1 h and the concentration of **7** appeared to level off after 2 h. The tube was attached to a vacuum line and all liquids as well as most of any remaining TCNE were pumped away overnight at high vacuum. The residue was extracted with cold ethanol-free $CHCl_3$, the solution filtered under N_2, and the solvent evaporated without warming to afford 80 mg of **7** as off-white crystals: ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.80 (d, J = Hz, 1 H), 5.65 (d, J = 8 Hz, 1 H), 5.15 (m, 1 H), 4.30 (s, 1 H, $CH(CN)_2$), 2.5–3.0 (m, 2 H), 1.82 (t, J = 1 Hz, 3 H, allylic CH_3), 1.10 (d, J = 7 Hz, 3 H, CH_3); IR (KBr pellet) 3020, 2960, 2890, 2250, 1660, 1450, 1400, 1270, 860 cm^{-1}. The product decomposes if heated above 50 °C or simply on standing at room temperature for some days, is air-sensitive when in solution, and does not survive chromatography of any kind. The only thermal decomposition products observable are *p*-xylene and tetracyanoethane; both were isolated and identified since the compound was too unstable for an analysis to be obtained.

3,3-Dimethyl-6-(1,1,2,2-tetracyanoethyl)-1,4-cyclohexadiene (8). A 5-mL ampule was charged with 440 mg of TCNE, 395 mg of diene **6**, and 1 mL of CH_3CN. After degassing (freeze–pump–thaw cycling) the ampule was sealed and placed in an oil bath at 65 °C for 135 h. The cooled ampule was opened, and the contents were transferred to a small flask and pumped on at 10^{-3} mmHg to remove all volatiles as well as much of the unreacted TCNE. Under a nitrogen blanket, the residue was stirred with several portions of ethanol-free $CHCl_3$ and the liquid filtered under nitrogen. The volume was reduced to 4 mL under reduced pressure without heating, 2 mL of hexane was added, and the solution was cooled to −15 °C. The resulting pink crystals were collected and dried. A second crystallization of these from CCl_4 gave white **8**, 110 mg, mp 97–99 °C dec: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.20 (dd, J = 10, 1 Hz, 2 H), 5.65 (dd, J = 10, 3.5 Hz, 2 H), 4.40 (s, 1 H), 3.65 (m, 1 H), 1.25 (s, 3 H), 1.15 (s, 3 H). [The signal at δ 4.40 shifts to 2.90 in acetone-d_6]; IR (KBr pellet) 3010, 2960, 2920, 2860, 2270, 1680, 1480, 1470, 1450, 1380, 1360, 920, 880, 820 cm^{-1}; UV (cyclohexane) λ_{max} 205 nm (ε 4700). Anal. Calcd for $C_{14}H_{12}N_4$: C, 67.91; H 5.70; N, 26.40. Found: C, 67.70; H, 5.73; N, 26.33. The mother liquor from the $CHCl_3$–hexane crystallization was evaporated to dryness and extracted with CCl_4. Cooling to −5 °C gave another 103 mg of somewhat less pure **8**.

Although no other adducts could be isolated, there are additional small NMR signals visible during the reaction of **6** and that we estimate would account for 2–3% of the diene consumed. Some of these signals decay at nearly the same rate that **8** does. Others are stabler.

1,3,3,4,6,6-Hexadeuterio-1,3-cyclohexadiene (2-d_6). Octadeuterio-1,4-cyclohexanedione, 98.9% deuteriated by mass spectroscopy (93.1 d_8), was prepared by the method of Bailey and Lambert[26a] and reduced to the diol with $LiAlH_4$ in analogy to the procedure of Karel et al.[26b] The diol was converted to the bistosylate by the same procedure used in the synthesis of **6**. A double elimination was carried out in the same way as for **6** to give a 30% yield of a 2:1 mixture of the hexadeuterio-1,3- and -1,4-cyclohexadienes. After removal of most of the pentane by slow distillation through a 10-cm Vigreux column, the products were distilled trap-to-trap and then separated by preparative gas chromatography at 40 °C on a $^1/_4$ in. × 10 ft column of 5% DEGS on 80/100-mesh acid-washed Chromosorb P.

NMR Kinetic Procedure. Two methods of sample preparation were used for the diene–TCNE reactions; one for the (faster) reactions with **3** and **5** in both CD_3CN and dioxane-d_8 and for **2** and **4** in CD_3CN and a slightly different one for the (slower) reactions of **6** in both solvents and **2** in THF and **4** in dioxane-d_8. All runs were done in duplicate. Most runs were carried out with a slight excess of TCNE. With **4**, initial concentrations were varied from a twofold excess of diene to a threefold excess of TCNE. The variation in the observed rate constants among these runs was less than the range found for many duplicate runs and showed no trend.

For the faster reactions, the diene was weighed into a 1-mL volumetric flask, solvent was added to near the mark, and the flask was placed in a 35 °C water bath. After it had sat for some time, additional solvent was added to the mark. In a second 1- or 2-mL volumetric flask, sublimed TCNE and *m*-dinitrobenzene were weighed and solvent added in the same manner as for the diene flask. An NMR tube was placed in the water bath. Two 0.5-mL syringes were warmed to 35 °C and fixed volumes of the two solutions transferred to the NMR tube, mixed, the starting time noted, and the sample placed in the T-60 NMR probe. Integrals and a few spectra were taken as rapidly as possible for **5** and for **3** in CD_3CN and at appropriate intervals in other cases where reaction was slower. Except for **5**, which reacted too quickly, at least 10 points were always recorded for diene disappearance and when the lifetimes of the intermediate were extended, an additional 10 to 15 points as well.

For the slower set of reactions, diene, TCNE and dinitrobenzene were all weighed into the same flask, the flask was filled to the mark at 35 °C, and the solutions were transferred to jointed NMR

(38) Pelletier, S. W. *Chem. Ind. (London)* **1953**, 1034.

tubes. The tubes were degassed by freeze–pump–thaw cycling and sealed. An initial NMR spectrum and integral were taken, the tube was placed in a water bath thermostated at 35 ± 0.1 °C, and spectra and integrals were taken through at least 2 half-lives of the diene (a 6-month period in some cases).

For the decompositions of the isolated adducts **1**, **7**, and **8**, a very similar procedure was used. *m*-Dinitrobenzene and then the adduct were weighed into a volumetric flask, the flask was warmed to 35 °C, and solvent was added to the mark with the time noted. For **1** and **7**, reaction was rapid enough to be run in a capped NMR tube, but with **8** the prolonged reaction time mandated that the tube be sealed (after degassing).

Isotope Effect Determination. Because we had only a very small amount of the deuteriated diene, the NMR kinetic method was not easily applicable. An HPLC procedure for following the reaction in more dilute solution (five- to tenfold in both reactants) was used. It allowed determination of both diene disappearance and benzene appearance rates, but not adduct concentrations. Into a 2-mL volumetric flask were weighed 20 to 30 mg of nitrobenzene and 40 to 60 mg of TCNE. The flask was half filled with acetonitrile and then 6 to 12 mg of the diene was weighed in, and the flask was rapidly filled to the mark and shaken to mix the reactants. The stopper was replaced with a serum cap and the flask placed in a 35 °C water bath. Periodically, 10-μL samples were withdrawn by syringe and immediately diluted 20:1 with ice-cold CH_3CN. Injection on a 25 cm × $^1/_4$ in. ODS reversed phase column and elution with 2:1 CH_3CN:water at a 1.5 mL/min flow rate separated the nitrobenzene standard (t_R 2.6 min), the benzene (3.1 min), and the unreacted diene (3.9 min). Any adduct peak present was not separated from the combined TCNE and tetracyanoethane peaks (1.5 min). Repeated injections of the chilled solutions showed that no significant reaction of either the initial reactants or any adduct took place following the 20:1 dilution and chilling during the time period needed to analyze duplicate injection samples. Peak areas (monitored at 215 nm) were quantitated on a Hewlett-Packard 3390A integrator. Areas were converted to concentrations by using previously determined response factors for diene and benzene versus the nitrobenzene standard.

The rate constant for disappearance of undeuteriated diene was twice remeasured by the same procedure and agreed with the NMR rate within 10%. Because the adduct itself could not be quantitated and the long reaction time needed with the deuteriated diene allowed some loss of benzene through the serum caps, no quantitative determination of the isotope effect on F or on adduct decomposition could be made.

Calculations. Calculations for rate of diene disappearance were always based on points over at least 2 but usually no more than 3 half-lives. Using the *m*-dinitrobenzene (or nitrobenzene in the HPLC method) internal standard, integrals were converted to concentrations and a linear least-squares fit was made by using the standard integrated form of the second-order rate equation.[39] Calculations for decomposition of the adducts were done similarly, using the standard first-order-integrated rate equation. For the curve-fitting calculations, a BASIC program was written to integrate numerically (Simpsons rule) the differential form of the series rate equations (second order followed by first order) using the initial concentrations of reactants from each run, the measured second-order rate constant, the measured, or for **4** and **5** estimated, first-order rate constant, and a fractional multiplier to divide the product of the first step between direct aromatization and adduct formation. The time period of the reaction was divided into 5000 intervals for the integrations. The multiplier, and when estimated, first-order rate constant were varied independently until the plots of calculated concentrations matched the experimental ones as closely as possible.

As noted in the introduction, we were initially concerned that CT complex formation would distort the kinetics and render the calculations untrustworthy. Several circumstances combined to render any curvature too small to be seen at the level of precision of NMR measurement of rates. The charge-transfer equilibrium constants (K_a) for the dienes are quite small. Haselbach measured one for **2** as 0.06 M^{-1} in CH_2Cl_2.[6] Although the constants are nearly 10 times larger for the arenes,[40] in many of the reactions not much arene forms until the diene has been virtually consumed, because under our high concentration conditions adduct formation is much faster than is its breakdown. Moreover, the term with P_f in eq 1 or 2 increases as the terms with A_f and D_f decrease so that the denominator as a whole will change more slowly.

Finally, and probably the dominant reason for the negligible curvature, both acetonitrile and dioxane themselves form CT complexes with TCNE. Ewall and Sonnessa showed that, as should be expected, the apparent equilibrium constant for the complex between benzene and TCNE declined substantially in CH_2Cl_2 from its value in CCl_4.[41] The TCNE–CH_2Cl_2 complex has a K_a of only 0.31 M^{-1}.[41] The complexes with acetonitrile and dioxane have K_a's of 2.13 M^{-1} and 1.92 M^{-1} (at 25 °C), respectively,[42] so that the apparent equilibrium constants for dienes dissolved in them would be reduced further. Altogether, this produces a denominator in the rate expression for k_{obs} that we did not expect to vary significantly under our experimental conditions.

To assure ourselves this would be so, we did the following "worst case" calculation. We solved numerically the simultaneous equilibrium equations

$$K_a = \frac{[DA]}{([A_t] - [DA] - [PA])([D_t] - [DA])}$$

and

$$K_b = \frac{[PA]}{([A_t] - [DA] - [PA])([P_t] - [PA])}$$

(which together constitute a cubic equation) for [DA] and [PA]. We substituted our experimental values of total diene, TCNE, and arene concentrations ($[D_t]$, $[A_t]$, and $[P_t]$) at 0, 1, and 2 half-lives, used the larger, CCl_4 solution equilibrium constants for the arene complexes, and assumed equilibrium constant values for the diene–TCNE complexes of **2**, **3**, and **5** that matched those measured for **2** in CH_2Cl_2. We used zero as the K_a value for **4** and **6** because we have been unable to see any charge-transfer bands in acetonitrile for **4** and **6**, probably because steric hindrance further decreases complex formation. Upon inserting the calculated CT complex concentrations in eq 1 or 2, the denominator was found to vary by less than 5% during 3 half-lives for the reactions of **2**, **3**, and **5**, by 9% in the reaction of **4** and by 11% for **6**. As we have found concentrations and rate constants determined from NMR integration data to vary by this much for some simple duplicate runs, we are not sure even this worst-case variation would be noticeable. Finally, to assure ourselves that the acetonitrile or dioxane were competing effectively with the dienes and arenes for TCNE, making the changes in the denominator of k_{obs} even smaller, we compared the UV spectra of several solutions of benzene plus TCNE in CH_2Cl_2 with those in acetonitrile. At concentrations of TCNE and benzene that were the same in the two solvents, the absorbance for the charge-transfer band was cut by over a factor of 3. Benesi–Hildebrand plots[43] (of admittedly rather limited accuracy) showed a decrease in the slope (= $K\epsilon$) by a factor of 6. We are thus confident that C-T complex formation produced no observable distortion of our rate plots.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. B.M.J. would also like to thank Prof. E. S. Lewis for his hospitality at Rice University where the isotope effect work was done and most of this manuscript was written. We also thank Ms. Motria Huk and Ms. Beatriz Mendez for their work on preparing some of the dienes used and Ms. Kristi

(39) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; John Wiley & Sons: New York, 1961; p 17.

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Reduction of Arenediazonium Salts by Hydroquinone. Kinetics and Mechanism for the Electron-Transfer Step

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Arenediazonium tetrafluoroborate salts undergo facile electron transfer reactions with hydroquinone in aqueous phosphate-buffered solutions containing the hydrogen donor solvent acetonitrile. Reaction rates are first-order in hydroquinone and arenediazonium ion concentrations, and they exhibit inverse first order dependence on the hydrogen ion concentration over the pH range of 1.0–9.5. Benzoquinone and arene are the principal products, but arylation of acetonitrile and benzoquinone are competitive in a reaction process that exhibits a 2:1 stoichiometric relationship between the arenediazonium ion salt and hydroquinone. Rate constants for reduction of substituted benzenediazonium ions by the monoanion of hydroquinone correlate with σ constants yielding a ρ value of 3.5. Reactions performed in deuterium oxide show kinetic isotope effects that reflect the solvent isotope effect on the acidity constant for hydroquinone, and levels of isotope incorporation by deuterium abstraction from deuterium oxide and/or acetonitrile-d_3 demonstrate that neither water nor hydroquinone are hydrogen atom donors to intermediate aryl radicals. Reduction of arenediazonium ions involves a rate-limiting single electron transfer from the monoanion of hydroquinone followed by a rapid single electron transfer from the semiquinone intermediate to the diazonium ion. Application of Marcus theory provides calculated rate constants for electron transfer from the hydroquinone monoanion to arenediazonium ions. These rate constants, together with the absence of evidence for a diazo ether intermediate and rate constants for diazotate formation, suggest that electron transfer occurs by an outer-sphere mechanism.

Hydroquinone/*p*-benzoquinone is a classic example of a redox-reversible organic system,[1,2] capable of undergoing the net two-electron transfer in one elementary step[3] or in two one-electron steps.[4-6] Both mechanistic events have been reported in extensive investigations of hydroquinone oxidations by a variety of metal complexes.[3-7] These reactions generally conform to outer-sphere electron transfer processes, although inner-sphere reactions have also been reported.[8]

Arenediazonium salts are highly susceptible to reduction[9] via one-electron transfer processes that may take either of two dynamic forms: a "nonbonded" outer-sphere mechanism involving the direct transfer of one electron from a reducing agent (Red:$^-$) to the diazonium ion (eq 1) and a "bonded" inner-sphere mechanism involving the formation of an intermediate complex (1) which undergoes homolytic cleavage (eq 2).[10] Both pathways result in the same products, and rapid loss of dinitrogen from the aryldiazenyl radical provides these pathways with their characteristic irreversibility. Unlike hydroquinone oxidations, whose reaction mechanisms are relatively well defined, there are few thorough kinetic investigations of the reductions of arenediazonium salts,[11-14] despite their synthetic uses.[15-17] Most reductive transformations of arenediazonium salts that have been investigated in detail are portrayed by inner-sphere mechanisms.[18] However, we have recently defined the characteristics of their outer-sphere electron-transfer processes through redox reac-

$$ArN_2^+ + Red:^- \rightarrow ArN_2^{\bullet} + Red^{\bullet} \quad (1)$$

$$ArN_2^+ + Red:^- \rightleftharpoons \underset{\mathbf{1}}{ArN{=}NRed} \rightarrow ArN_2^{\bullet} + Red^{\bullet} \quad (2)$$

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