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A Study of Valence Tautomerism of Cycloheptatriene-Norcaradiene

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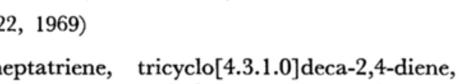
Rates of the Diels-Alder reaction of cycloheptatriene, tricyclo[4.3.1.0]deca-2,4-diene, 1,3-cyclohexadiene, and *cis*-bicyclo[4.3.0]nona-2,4-diene with excess of fumaryl chloride were measured using a dilatometer. Comparison of the rate of cycloheptatriene with that of other olefins raises the question of the free energy difference so far estimated between cycloheptatriene and norcaradiene, which has been proposed to exist in equilibrium. It is suggested that the most preferable mechanism of the Diels-Alder reaction of cycloheptatriene is not through the norcaradiene isomer, but through the transition state of the norcaradiene structure.

The valence tautomerism of unsaturated medium ring systems is of current interest,[1] and recent studies have indicated that cyclooctatetraene,[2] cyclooctatriene[2,3] and oxepine[4] are in equilibrium with their tautomeric isomers, bicyclo[4.2.0]octa-2,4,7-triene, bicyclo[4.2.0]octa-2,4-diene, and benzene oxide, respectively. In this kind of study for cyclooctatriene, the major technique was a kinetic study of the Diels-Alder reaction.[2] Regarding tropilidene, the spectroscopic studies have indicated that the principal species is 1,3,5-cycloheptatriene, whereas the product studies of the chemical reactions have suggested that norcaradiene is the reacting species.[5] The reaction of tropilidene with dienophile yields tricyclic products containing a cyclopropane ring formally derived from norcaradiene,[6] and the thermal isomerization of tropilidene gave toluene formed, presumably, by cleavage of the three-membered ring of norcaradiene.[7] For about twenty years, the chemistry of tropilidene and related compounds has been actively carried out in Japan.

These circumstances prompted us to carry out a kinetic study of the Diels-Alder reaction of tropilidene with fumaryl chloride[6a] in the hope that the norcaradiene isomer hypothetically existing in equilibrium with cycloheptatriene could be demonstrated.[8]

Kinetic Problem.



A B D C

If we assume an equilibrium ($K=k_1/k_{-1}$) between cycloheptatriene (A) and norcaradiene (B), followed by the Diels-Alder addition of B to a dienophile (D), that is a two-step mechanism, the rate of the adduct (C) formation, d[C]/dt, is denoted by k_2[B][D]. Setting d[B]/dt=0 from steady state approximation, we have

$$\mathrm{d[B]/d}t = k_1[\mathrm{A}]-k_{-1}[\mathrm{B}]-k_2[\mathrm{B}][\mathrm{D}] = 0$$

$$[\mathrm{B}] = k_1[\mathrm{A}]/(k_{-1}+k_2[\mathrm{D}])$$

$$\mathrm{d[C]/d}t = k_2[\mathrm{B}][\mathrm{D}] = k_1k_2[\mathrm{A}][\mathrm{D}]/(k_{-1}+k_2[\mathrm{D}]) \qquad (1)$$

Under the condition that the concentration of D is much larger than that of A, the concentration of D is constant throughout the reaction period.

$$k_1k_2[\mathrm{D}]/(k_{-1}+k_2[\mathrm{D}]) = k_c \qquad (2)$$

k_c is the pseudo-first order rate constant varying with [D], and one can get the following equation.

$$\mathrm{d[C]/d}t = k_c[\mathrm{A}]$$

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[1] As recent reviews, a) E. Vogel, *Angew. Chem.*, **74**, 829 (1962); b) S. J. Rhoad, "Molecular Rearrangements," Vol, 1, ed. by P. de Mayo, John Wiley & Sons, New York, N. Y. (1963), p. 655.

[2] R. Huisgen, F. Mietzsch, G. Boche and H. Seidl, "Organic Reaction Mechanisms," The Chemical Society, London (1965), p. 3.

[3] a) A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952); b) D. S. Glass, J. Zirner and S. Winstein, *Proc. Chem. Soc.*, **1963**, 276.

[4] E. Vogel and H. Günther, *Angew. Chem. Internat. Edit.*, **6**, 385 (1967).

[5] G. Maier, *ibid.*, **6**, 402 (1967); references cited therein.

[6] a) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953); b) K. Alder, K. Kaiser and M. Schumacher, *Ann.*, **602**, 80 (1957); c) K. Alder, H. Jungen and K. Rust, *ibid.*, **602**, 94 (1957).

[7] a) K. N. Klump and J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 130 (1963); b) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

[8] Interest in the kinetic studies of the Diels-Alder reactions was stimulated by the lecture given by Professor R. Huisgen at the Shionogi Research Laboratory in March 1962, and personal discussions one of the authors had with him later in October 1967. Our thanks are due to Professor Huisgen.

According to the magnitude of k_1,k_{-1} and k_2, the situation is further divided into three cases.

(a) $k_2[D] \ll k_1$ and k_{-1}. The slow combination of B with D compared to the rapid equilibrium is rate-determining. From Eqs. (1) and (2) we have $d[C]/dt=(k_1/k_{-1})k_2[A][D]$ and $k_c=(k_1/k_{-1})k_2[D]$.

(b) $k_2[D] \gg k_1$ and k_{-1}. The first equilibrium step becomes the rate-determining step. $d[C]/dt=k_1[A]$ and $k_c=k_1$.

(c) $k_2[D] \approx k_1$ and k_{-1}. This case corresponds to that between the two limiting cases (a) and(b), and both steps are effective on rate-determination. The relation is represented by Eqs. (1) and (2).

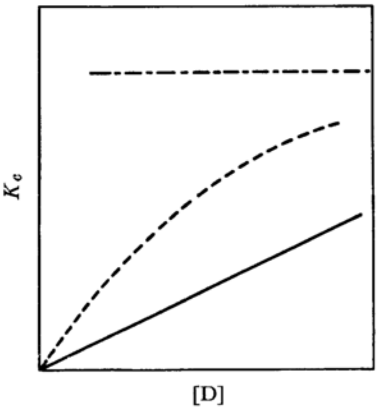


Fig. 1. Correlation of K_c and $[D]$.
—— Case (a) and (d)
---- Case (c)
—·—·— Case (b)

Plotting k_c against the varying amounts of D, as shown in Fig. 1, provides, for the case (a), a straight line through the origin having a slope of $(k_1/k_{-1})k_2$, for (b), a straight line parallel to the abscissa corresponding to $k_c=k_1$, and for (c), a curve through the origin.

The case (d): if the Diels-Alder reaction proceeds without intervention of B and produces C with the second order rate constant of k_2', we have

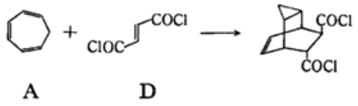
$$d[C]/dt = k_2'[A][D]$$

When the concentration of D is much larger than that of C, we have $d[C]/dt=k_c'[A]$ where $k_c'=k_2'[D]$. This relation should be the same as the case (a).

Results

The kinetic studies were performed under such conditions that the concentration of fumaryl chloride⁹⁾ varied from ten to thirty times the concentration of cycloheptatriene. The rate was followed dilatometrically in dioxane by measuring the reduction in the total reaction volume due to the union of the two molecules to one.¹⁰⁾ A decrease of the meniscus height in the graduated capillary against the reaction time satisfied the correlation of the pseudo-first-order up to about three half-lives. As an example, rate constants, k_{obs} at 55.01°C, varying the concentration of fumaryl chloride are shown in Table 1.

TABLE 1. THE DIELS-ALDER REACTION OF CYCLOHEPTATRIENE WITH FUMARYL CHLORIDE



$[A]\times10^2$ mol/l	[D] mol/l	[D]/[A]	$K_{obs}\cdot$ sec^{-1}
6.01	0.63	10.4	5.54×10^{-5}
6.01	1.20	20.0	1.16×10^{-4}
6.01	1.51	25.0	1.44×10^{-4}
6.01	1.79	29.8	1.84×10^{-4}

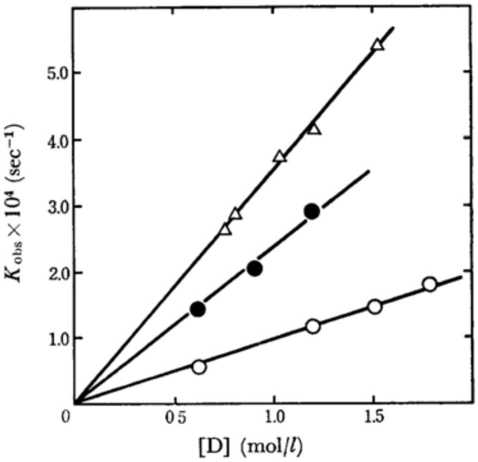


Fig. 2. Correlation of kobs and [D] at three temperatures.
○ 55.01°C ● 72.47°C △ 79.98°C

Plotting k_{obs} against increasing concentrations of fumaryl chloride at 55.01°C, 72.47°C and 79.98°C, yielded straight lines, as shown in Fig. 2. These linearities correspond either to the case (a) $k[D] \ll k_1$ and k_{-1} involving the intermediate (B), or the case (d) which is not through B. Similar lines were also obtained from the reaction with a more reactive dienophile, tetracyanoethylene.

Slopes of the straight lines represent the values of $(k_1/k_{-1})k_2$ or k_2' at the respective temperatures.

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9) Fumaryl chloride is a very reactive dienophile. Its addition to cyclopentadiene proceeds (at 20°C in dioxane) 100 times more rapidly than the addition of maleic anhydride to the same diene. J. Sauer, H. Wiest and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

10) R. Huisgen in "Methoden der Organischen Chemie," Vol. III, Part I, ed. by E. Muller, Georg Thieme Verlag, Stuttgart (1955), p. 120.

TABLE 2. RATES OF THE DIELS-ALDER REACTION OF CYCLOHEPTATRIENE WITH FUMARYL CHLORIDE

Temp. °C	$(k_1/k_{-1})k_2$ or k_2' (l/mol·sec)	Calculated at 15°C		
		$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/deg)	$(k_1/k_{-1})k_2$ or k_2' (l/mol·sec)
55.01	1.08×10^{-4}			
72.47	2.50×10^{-4}	10.8	−44	$9.7\times10^{-6\,a)}$
79.98	3.69×10^{-4}			

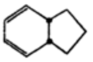
a) Calculated from the observed rates using the least square method.

Table 2 shows their values and the value extrapolated to 15°C by use of the Arrhenius equation.

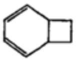
If the Diels-Alder reaction of cycloheptatriene proceeds through an equilibrium with B, since $(k_1/k_{-1})k_2$ is now known, evaluation of k_2 leads to a determination of the equilibrium constant (k_1/k_{-1}). We wanted to evaluate k_2 from the Diels-Alder reactions of some compounds, which are structually related to norcaradiene, with fumaryl chloride. The compounds chosen were tricyclo[4.3.1.0]deca-2,4-diene (E),[11] 1,3-cyclohexadiene (F), *cis*-bicyclo[4.3.0]nona-2,4-diene (G), and bicyclo[4.2.0]octa-2,4-diene (H), in which E has the norcaradiene structure fixed by an additional five-membered ring.

E

F



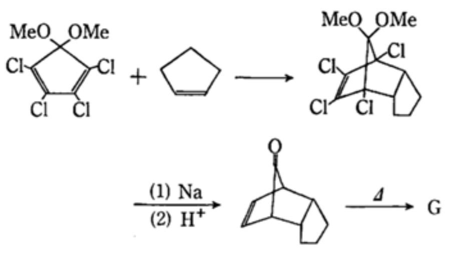
G



H

G was prepared by us according to the schema shown below, although it had been synthesized by Alder through a different route.[12]

Under the conditions of the pseudo-first-order with excess of fumaryl chloride, the addition rates of the dienes were determined in the same way as above and summarized in Table 3.



Discussion

If the cycloheptatriene-norcaradiene pre-equilibrium exists, the overall rate of the adduct formation from cycloheptatriene is shown as $(k_1/k_{-1})k_2=9.7\times10^{-6}$ l/mol·sec at 15°C. The second-order rate constants, k_E, k_F, k_G and k_H, obtained from E, F, G and H, respectively, are given in Table 4. Here, k_H was estimated on the fact that the addition of H to maleic anhydride is thirty times faster than that of cyclohexadiene (F) in dioxane at 30°C (by Huisgen[2]) and Sauer[13])).

TABLE 4. ASSUMED EQUILIBRIUM BETWEEN CYCLOHEPTATRIENE AND NORCARADIENE[a)]

Compd.	k_2 (l/mol·sec)[b)]	k_1/k_{-1}[c)]	Norcaradiene at equilibrium (%)
E	1.2×10^{-5}	0.8	45
F	4.7×10^{-4}	2×10^{-2}	2
G	9.5×10^{-3}	10^{-3}	0.1
H	1.4×10^{-2}	7×10^{-4}	0.07

a) At 15°C.
b) Rate of the Diels-Alder reaction of the dienes with fumaryl chloride at 15°C (Table 3).
c) Calculated from the equation $(k_1/k_1)k_2=9.7\times10^{-6}$ l/mol·sec.

TABLE 3. RATES OF THE DIELS-ALDER REACTION OF VARIOUS DIENES WITH FUMARYL CHLORIDE

Compd.	Temp. °C	K (l/mol·sec)	Calculated at 15°C		
			$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/deg)	K (l/mol·sec)
E	45.00	$8.24\times10^{-4\,a)}$	11.0	−43	$1.2\times10^{-5\,a,d)}$
	32.60	$3.98\times10^{-4\,a)}$			
	19.97	$1.77\times10^{-4\,a)}$			
F	25.42	$9.62\times10^{-4\,b)}$	11.2	−35	$4.7\times10^{-4\,b,d)}$
	15.00	$4.48\times10^{-4\,b)}$			
	15.02	$4.97\times10^{-4\,b)}$			
G	15.00	$9.50\times10^{-3\,c)}$			$9.5\times10^{-4\,c)}$

a) K_E. b) K_F. c) K_G.
d) Calculated from the observed rates using the least square method.

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[11] E. Vogel, W. Wiedemann, H. Kiefer and V. F. Harrison, *Tetrahedron Letters*, **1963**, 673.

[12] K. Alder and H. A. Dortmann, *Chem. Ber.*, **87**, 1905 (1954).

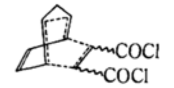
[13] J. Sauer, D. Lang and A. Mielert, *Angew. Chem. Internat. Ed.*, **5**, 211 (1966).

Replacement of k_2 by these second-order constants yields various estimations of k_1/k_{-1}, from which the equilibrium concentrations of norcaradiene are derived as 45, 2, 0.1 and 0.07% (Table 4). However, the former two values could be eliminated, because they are very unreasonable on the basis of the spectral properties of tropilidene reported.[5] Appropriate adoptions of the latter two values lead to the free energy differences of 4.0 and 4.5 kcal/mol respectively, existing between cycloheptatriene and norcaradiene.

On the other hand, the free energy difference of 11±4 kcal has been proposed[14] basically from the table of bond-energy[15] and some discussions using this value have appeared frequently in literatures.[16] The value of 11±4 kcal/mol corresponds to k_1/k_{-1} of 5×10^{-6}—4×10^{-12}. Thus, introduction of this k_1/k_{-1} value into the equation, $(k_1/k_{-1})k_2 = 9.7\times10^{-6}$ l/mol·sec, yields k_2 of 2—2×10^6 l/mol·sec as the addition rate of norcaradiene to fumaryl chloride at 15°C, which turns out to be an astonishingly large value referring to the second-order rate constants of E, F, G and H. Even the lowest value, 2 l/mol·sec, which corresponds to the free energy difference of 7 kcal/mol, is close to the rate of highly reactive cyclopentadiene with fumaryl chloride at 20°C in dioxane.[9] These lead to two alternative views; (i) the rate of the Diels-Alder reaction of norcaradiene is abnormally larger than we would expect on the basis of present organic theories, or (ii) the estimated value of 11±4 kcal/mol is unreasonably large.

By comparison of the rate of G with that of F (Table 3), it might be considered that a fused five-membered ring accelerates the Diels-Alder reaction by a factor of twenty. If view (i) is taken, it is reasonable to regard that Vogel's compound (E) fusing a five-membered ring to the norcaradiene structure has also a great reactivity in the Diels-Alder reaction. However, it is found that E is less reactive by a factor of forty than F. Although there was no evidence that the reactivity of E should be compatible with that of norcaradiene, these discrepancies throw a serious doubt upon the free energy difference of 11±4 kcal/mol.

Consequently, three basic limiting cases are derived for the relationship between cycloheptatriene and norcaradiene. (1) The free energy difference between both structures is much smaller than the previously proposed value of 11±4 kcal/mol. (2) The difference of 11±4 kcal/mol exists and then the addition rate of norcaradiene is abnormally great by presently unknown factors. (3) The Diels-Alder reaction of cycloheptatriene does not proceed through norcaradiene which has been proposed to exist in the ground state, but takes the norcaradiene structure in the transition state, pictured as



Although available data are insufficient to obtain a conclusion on the above alternatives, we prefer the possibility of (3) that transition into norcaradiene takes place only under the influence of the attacking agent.

Experimental

All melting points were corrected. Infrared spectra were recorded on a Nippon Bunko IR-S spectrometer. NMR spectra were determined at 60 Mc with a Varian A-60 Spectrometer using tetramethylsilane as an internal standard.

Materials and Apparatus. The cycloheptatriene used in this work was Shell chemical material which was obtained in a purity better than 95% by distillation (bp 114—115°C). Tricyclo[4.3.1.0]deca-2,4-diene (E), bp 71—73°C/15 mmHg, n_D^{24} 1.5248 (lit.[11] bp 61—62°C/11 mmHg, n_D^{20} 1.5267) was prepared by the procedure of Vogel. 1,3-Cyclohexadiene (F) (bp 79—80°C) was supplied by Dr. T. Nakata.[17] Dioxane was purified by the procedure of Hess and Frahm.[18]

The dilatometer used, whose desigh is explained in Ref. 10, is equipped with a reaction vessel of about 20 cc and a graduated capillary of inner-diameter of 0.5 mm. Thermostat was maintained in a range of ±0.01°C at the indicated temperatures.

Typical Rate Determination. The sample of 1.385 g of cycloheptatriene was weighed in a 20 ml volumetric flask and filled to 20 ml with dioxane. Fumaryl chloride (4.590 g) was accurately weighed in a 25 ml volumetric flask, to which *ca.* 20 ml of dioxane and an aliquot of 2 ml from the dioxane solution of cycloheptatriene previously prepared was added. The mixed solution was kept in thermostat at 55.01°C for a short time and filled to 25 ml with dioxane, so that the concentrations of cycloheptatriene and fumaryl chloride were 0.0601 and 1.200 mol/l. After cooling, the resulting solution was transferred into the dilatometer, whose meniscus in the capillary was adjusted to the desired height when the thermostat attained the reaction temperature. Then reading of the meniscus height was started and continued until ten-half lives. The difference in the meniscus height from start to ten-half lives was 6.67 cm.

Addition of Tetrachlorocyclopentadienone Dimethyl Ketal to Cyclopentene. A mixed solution of 10 g of cyclopentene and 41.7 g of tetrachlorocyclopen-

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[14] W. von E. Doering and M. R. Willcott, III, unpublished; M. R. Willcott, III, Ph. D. Dissertation, Yale University, 1963.

[15] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

[16] a) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966); b) G. D. Sargent, N. Lowrry and S. D. Reich, *ibid.*, **89**, 5985 (1967).

[17] T. Nakata and N. Choumei, *J. Macromol. Sci-Chem.*, **A1(8)**, 1433 (1967).

[18] K. Hess and H. Frahm, *Ber.*, **71B**, 2627 (1938).

tadienone dimethyl ketal was sealed in a glass tube and heated to 170°C for 18 hr. After cooling, the solid residue was chromatographed on 100 g of standard Merck alumina with petroleum ether (bp 40—50°C) to exclude dark brown impurity. The eluent was concentrated. The residue solidified was recrystallized from petroleum ether to give 40.1 g (82.3% based on cyclopentene) of *endo*-1,7,8,9-tetrachlorotricyclo[5.2.1.$0^{2,6}$]deca-8-en-10-one dimethyl ketal, mp 83.5—84.5°C. NMR (CCl_4) at τ 6.44 and 6.52 (two methoxyls, 6H, singlet), 7.0 (two methines, 2H, multiplet) and 7.57 (three methylenes, 6H, multiplet). Found: C, 43.69; H, 4.27%. Calcd for $C_{12}H_{14}Cl_4O$: C, 43.41; H, 4.25%.

***endo*-Tricyclo[5.2.1.$0^{2,6}$]deca-8-en-10-one.** A solution of 33.2 g of the above adduct in 600 m*l* of tetrahydrofuran and 96.5 g of *t*-butyl alcohol was efficiently stirred at reflux temperature under nitrogen atmosphere. Sodium chip (57.5 g) was cautiously added for over one hour to the reaction mixture followed by stirring for an additional 5 hr. After cooling, the remaining sodium was decomposed with cold methanol and then with a large amount of cold water. The solution was extracted with ether, dried over sodium sulfate, and evaporated to yield 19.0 g of an oily residue, which was distilled at 98—103°C /8 mmHg to give 14.0 g of the dechlorinated ketal.

The ketal was dissolved in 30 m*l* of methanol and 50 m*l* of 70% aqueous acetic acid, and warmed to 80°C under stirring for 3.5 hr. The reaction mixture was poured into cold water and made alkaline with sodium hydroxide. After extraction with ether, evaporation gave 9.8 g of a solid residue, which was recrystallized from petroleum ether to give 8.5 g (57.5%) of white needles, mp 61.5—63.0°C (in sealed tube). NMR (CCl_4) at τ 3.62 (vinyl, 2H, triplet), 7.1 (two methines, 2H, at carbon 1.7, quintet), 6.58 (two methines at carbon 2.6, multiplet), and 8.0—9.2 (three methylenes, 6H, multiplet). IR $\nu_{max}^{CCl_4}$ 2985, 2940, 2858, 2866, and 1782 cm^{-1}. Found: C, 81.29; H, 8.20%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

***cis*-Bicyclo[4.3.0]nona-2,4-diene (G).** The ketone was vaporized at 120—130°C and reduced pressure (35 mmHg) in a stream of nitrogen introduced by means of a fine capillary tube. The vapor passed through a 30 cm section of 4 mm (diameter) tubing packed with glass grain of 30—40 mesh and maintained at 250—300°C by means of an externally heated coil of nichrome wire. The products were trapped at dry ice - acetone temperature. The crude pyrolysate was distilled at 101—102°C/123 mmHg to yield 4.5 g (79.2%) of the decarboxylated diene, n_D^{25} 1.5052. NMR (CCl_4) at τ 4.42 (vinyl, 4H, multiplet), 7.4 (two methines, 2H, multiplet) and 8.0—8.8 (three methylenes, 6H, multiplet). UV: $\lambda_{max}^{n\text{-heptane}}$ 260 mμ (ε 4200), IR $\nu_{max}^{CCl_4}$ 3030, 2942, 2868, 1640, 1585, 1449 and 690 cm^{-1}. Found: C, 89.95; H, 10.07%. Calcd for C_9H_{12}: C, 89.94; H, 10.06%.