

**Hydrogenation of the Cycloadducts of *trans-trans*-2,4-Hexadiene and 1,1-Dichloro-2,2-difluoroethylene.**—For this experiment an adduct was used which was prepared by heating for 47 hr. in an oven at 80–90°. The adduct, analyzed on an 8-ft. column, 0.25 in. o.d., packed with 20% 1,2,3-tris- $\beta$ -cyanoethoxypropane (helium flow 60 ml./min., 115°) contained isomers II and III in a ratio of 5.09 to 1 (retention times 14 and 18 min., respectively).

In 40 ml. of glacial acetic acid was dissolved 0.35 g. of the twice-distilled cycloadduct. To this was added 0.037 g. of commercial platinum oxide catalyst. The catalyst was not hydrogenated before addition of the adduct. The mixture was hydrogenated at 27° and 1 atm. pressure. In 20 min. 48 ml. of hydrogen was taken up and then the reaction stopped completely (theoretical hydrogen uptake:  $22.4 \times 0.35/2.5 \times 300/273 = 40$  ml.). The catalyst was removed by filtration and 200 ml. of water was added. The mixture was extracted seven times with 10-ml. portions of *n*-pentane. The solution was dried over magnesium sulfate and the *n*-pentane distilled off through a short Holtzmann column. The number and ratio of products was determined by v.p.c. (8 ft., 0.25 in. o.d., 20% 1,2,3-tris- $\beta$ -cyanoethoxypropane column, helium flow rate 60 ml./min., 130°). Two product peaks at 5 and 7 min. were found, the area under the

peaks having a ratio of 5.00:1 (the one with the shorter retention time is the larger).

**Hydrogenation of the Four-Component Adduct Mixture.**—By a similar procedure, 0.149 g. of a four-component mixture of adduct isomers was hydrogenated with 0.015 g. of commercial platinum oxide. The hydrogen uptake was 24.4 ml., complete in 45 min. In a blank experiment an equal weight of the catalyst took up 6.8 ml. of hydrogen. The uptake by the sample was therefore  $24.4 - 6.8 = 17.6$  compared with a theoretical 17.0.

In the analyses, isomers I and II were determined together in an imperfectly resolved peak at 34 min. on 1,2,3-tris- $\beta$ -cyanoethoxypropane and 47 min. on tricresyl phosphate. Isomer III had retention times on these columns of 42 and 59 min., and isomer IV of 48 and 63 min., respectively. The product had two peaks at 17 and 25 min., respectively, on the tris- $\beta$ -cyanoethoxypropane column. The ratio of the second to the first peak in three determinations was 0.229, 0.251, and 0.251, from an initial mixture with (III + IV)/(I + II) ratios of 0.237 and 0.223.

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### Cycloaddition. III. Kinetics and Reactivity in the Addition of 1,1-Dichloro-2,2-difluoroethylene to Dienes. The Biradical Mechanism

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In 1,2-cycloaddition of 1,1-dichloro-2,2-difluoroethylene to dienes, both 2-methyl and 2-chlorine substitutions are mildly activating for addition to the 1,2-double bond and deactivating for addition to the 3,4-double bond. *cis*-Piperylene is slightly more reactive than *trans*-piperylene. Terminal methyl substitution slows cycloaddition much as it does free radical polymerization. Cyclopentadiene is attacked 70% as fast as butadiene instead of being 1350 times as reactive, as it is toward maleic anhydride in the Diels–Alder reaction. These facts are regarded as consistent with the two-step biradical mechanism supported in parts I and II; and they emphasize that the mechanism of the Diels–Alder reaction is entirely different from that of addition of haloolefins, even when (as in the case of cyclopentadiene) the latter yield chiefly 1,4-addition products.

#### Introduction

One of the most direct ways to study the difference between the reaction of dienes with dienophiles (1,4-addition in the Diels–Alder reaction) and the reaction of the same dienes with 1,2-cycloaddition reagents would be to observe the effects of structural variations upon the rates of these two differing processes. It was shown in part I of this series that the orientation of an unsymmetrical reagent<sup>1</sup> such as 1,1-dichloro-2,2-difluoroethylene ("1122") is consistent with the hypothesis that the point of initial bond formation is that which leads to the most favorable biradical intermediate. It was shown in part II that cycloaddition to geometrically isomeric dienes proceeds through a stage permitting free rotation about the axis of the double bond to which the addition is taking place.<sup>2</sup> Although the addition reactions of typical dienophiles can be discussed in terms of a possible bifunctional intermediate,<sup>3</sup> the stereospecificity commonly associated with these reactions<sup>4</sup> indicates that, if biradicals are involved, they have rather different properties from the biradicals of ref. 2 and the possibility remains open that only one transition state is traversed by the reactants in the course of a Diels–Alder reaction.

In the present paper we have compared the rates of 1,2-cycloaddition of 1,1-dichloro-2,2-difluoroethylene to a series of dienes whose reactivities toward maleic anhydride have already been compared.<sup>5,6</sup>

(1) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964).

(2) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964).

(3) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(4) M. C. Kloetzel, "Organic Reactions," Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 1; H. L. Holmes, *ibid.*, Vol. 4, p. 60.

(5) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2884 (1961).

(6) J. Sauer, *Angew. Chem.*, **74**, 252 (1962).

#### Experimental

**Materials.**—The sources and preparations of the compounds have been described in parts I<sup>1</sup> and II.<sup>2</sup>

**Procedure for Kinetic Runs.**—Rate measurements were made employing an ampoule technique and following the rate of appearance of cycloadducts by vapor phase chromatography.

Ampoules having a capillary neck and a volume of 1.6–1.8 ml. were prepared from heavy-walled Pyrex tubing (12.7 mm. o.d., 2.3 mm. wall thickness) and were oven annealed. Another type of ampoule, which was used in making density measurements, had a second capillary constriction immediately above the first.

A concentrated solution of inhibitor (di-*n*-butylammonium picrate or hydroquinone) in methylene chloride was prepared. A volume of solution containing 10 mg. of inhibitor was added to each ampoule by syringe. The methylene chloride was removed under reduced pressure and the ampoules were stored in a desiccator until used. It was necessary to place the inhibitor in each ampoule rather than add it to the reactants, since the inhibitors used were of limited solubility in the cold reactants.

The solutions were prepared by weight in a vacuum-jacketed volumetric flask of about 15.0 ml. The solutions were 0.5–1.5 *M* in 1,3-diene and the 1,1-dichloro-2,2-difluoroethylene was employed as the solvent (8.0–8.5 *M*). Diene dimerization was minimized by using the fluoroolefin as solvent, which also permitted lower reaction temperatures. The dimer of 1,1-dichloro-2,2-difluoroethylene represented less than 0.3% of the reaction products at 80°. All of the components of the solutions were placed in an ice bath prior to weighing. The cooling facilitated the transfer of these liquids by syringes fitted with long needles.

The volumetric flask was weighed and cooled by washing with 1,1-dichloro-2,2-difluoroethylene. The diene (enough for 0.5–1.5 *M* solution) and the internal standard (purified toluene, cumene, or *t*-butylbenzene) were weighed out, and the solution was made up to 15.0 ml. with 1,1-dichloro-2,2-difluoroethylene. An amount of internal standard was added which provided a v.p.c. peak area corresponding to 40% of the peak area of the theoretical yield of cycloadduct. By adding the internal standard to the reactants it was possible to eliminate quantitative transfers and the large errors accompanying them.

About 1.2 ml. of the reactant solution was added to each of the standard ampoules and an amount to the modified ampoule which was just sufficient to bring the solution up into the capillary neck at the reaction temperature (the solution expanded about 10% upon being heated from 0 to 80°). The ampoules were sealed off at the capillary neck and placed in an oil bath maintained at

TABLE I  
 SUMMARY OF THE COMPETITIVE RATE STUDIES AT 81.87°

Toluene, mmoles	Isoprene, mmoles	Butadiene, mmoles	Chloroprene, mmoles	$(F_0)_I^b$	$(F_0)_D^c$	$\frac{A_I^d}{A_T}$	$\frac{A_D^d}{A_T}$	$\frac{k_D^d}{k_I}$
6.040	16.165	16.228		0.746	0.776	2.94	2.48	0.738
5.561	13.184		15.74	0.746	1.018 <sup>a</sup>	2.67	0.892 <sup>a</sup>	0.555

<sup>a</sup> The conversion factor between the isoprene adduct and the chloroprene adduct was used. <sup>b</sup>  $(F_0)_I$  = chromatographic proportionality constant  $F_0$  for isoprene adducts. <sup>c</sup>  $(F_0)_D$  = value of  $F_0$  for adduct of competing diene (butadiene or chloroprene). <sup>d</sup>  $A$ 's are areas under v.p.c. peaks; subscripts D, I, and T refer to competing diene, isoprene, and the toluene chromatographic standard, respectively.

78 ± 1° for 3 min. They were then removed and placed in a thermostated bath at 79.46 or 81.87 ± 0.03°. After 5–7 min. the modified ampoule was removed and zero time recorded. The level of the solution in the capillary neck was marked, and the reaction was quenched by shaking the ampoule in ice water for 30 sec. The ampoules were stored at –35° until they were analyzed. The inhibitor precipitated out at this temperature, but it was shown that the ratio of the internal standard to cycloadduct remained constant. The composition of quenched solutions did not change after several weeks of storage.

Analyses were carried out employing an F & M Model 300 gas chromatograph with a 1 mv. Minneapolis–Honeywell recorder equipped with a disk integrator. Columns (6 ft., 0.25 in. o.d.) were made of stainless steel and were packed (20%) with either diisodecyl phthalate or 1,2,3-tris-(2-cyanoethoxy)-propane on 60–80 mesh Chromosorb-P.

The first ampoule was opened at the upper capillary section, and the weight of the reaction products determined. The ampoule was cleaned, held at 79.46°, and refilled with distilled water. The density of the solution at 79.46° was determined, and the initial concentrations of the 1,3-diene,  $D_0$ , and the fluoroolefin,  $F_0$ , at  $t = 0$  were calculated.

The ratios of the peak areas of the cycloadducts to the internal standard were obtained with the aid of the disk integrator. If the areas were measured carefully (*i.e.*, the baseline zeroed and the maximum sample size used), a single v.p.c. determination gave acceptable accuracy, as judged by the agreement of duplicates.

The number of millimoles of cycloadducts and of standard,  $M_C$  and  $M_S$ , respectively, were determined from the corresponding v.p.c. peak areas  $A_C$  and  $A_S$  by the equation

$$M_C/M_S = F_0(A_C/A_S) \quad (1)$$

The proportionality constant  $F_0$  was determined by measuring the v.p.c. peak areas from known mixtures of adduct and internal standard. In the case of the isoprene cycloadducts it was shown that  $F_0$  was independent of the ratio  $M_C/M_S$ . From the initial amounts of diene and fluoroolefin ( $(M_D)_0$  and  $(M_F)_0$ ), and their initial concentrations  $D_0$  and  $F_0$  it was possible to apply the integrated second-order rate equation

$$\frac{1}{F_0 - D_0} \ln \left[ \frac{(M_F)_0 - M_C}{(M_D)_0 - M_C} \frac{(M_D)_0}{(M_F)_0} \right] = k_D t \quad (2)$$

Plots of  $\log [(M_F)_0 - M_C]/[(M_D)_0 - M_C]$  vs. time gave good straight lines through two half-lives;  $k_D$  was determined from the slopes of these lines.

**Competitive Rate Studies.**—Approximately 1 *M* solutions of butadiene or chloroprene and isoprene in 1,1-dichloro-2,2-difluoroethylene were prepared. Toluene was added as an internal standard and di-*n*-butylammonium picrate was used as a polymerization inhibitor. The experimental procedure differed little from that used for determining specific reaction rates. The reactions were thermostated for about 8 hr. at 81.87°, which corresponded to approximately two diene half-lives.

The butadiene, isoprene, and chloroprene cycloadditions are irreversible under the reaction conditions. No new reaction products were noted in competitive reactions, indicating that the diene pairs did not react with one another. Accordingly, the ratio of rate constants for the competing diene,  $k_D$ , and the isoprene,  $k_I$ , is given by

$$\frac{k_D}{k_I} = \frac{\log (D/D_0)}{\log (I/I_0)} = \frac{\log (M_D/(M_D)_0)}{\log (M_I/(M_I)_0)} \quad (3)$$

The results are shown in Table I.

**Competitive Rate Ratio of *cis*-1,3-Pentadiene and *trans-trans*-2,4-Hexadiene with 1,1-Dichloro-2,2-difluoroethylene.**—Duplicate samples consisting of 0.100 ml. of *cis*-1,3-pentadiene, 0.100 ml. of *trans-trans*-2,4-hexadiene, 1.50 ml. of 1,1-dichloro-2,2-difluoroethylene, and 5.0 mg. of di-*n*-butylammonium picrate were prepared and were heated in heavy-walled glass ampoules for 14.2 hr. at 80.05°. The ratios of the areas for the two types of cycloadducts,  $R_2$ , were determined by v.p.c. (8 ft., 0.25 in. o.d., 20% 1,2,3-(2-cyanoethoxy)-propane on 60–80 mesh Chromosorb-P; dienes at room temperature, 60 ml./min.; cycloadducts at 90°, 120 ml./min.).

A rough estimate of the ratio of the rate constant for *cis*-1,3-pentadiene,  $k_p$ , to that of *trans-trans*-2,4-hexadiene,  $k_H$ , was made with the use of several assumptions. First, it was assumed that equal molar quantities of the two dienes were present initially, since the differences in molecular weights and densities tend to cancel one another. Further, it was assumed that the thermal conductivities of the two dienes were identical and that those of the three cycloadducts were identical. If  $x$  is the fraction of unreacted *cis*-1,3-pentadiene and  $y$  is the fraction of unreacted *trans-trans*-2,4-hexadiene, both  $R_1$  and  $R_2$  may be expressed in terms of these quantities.

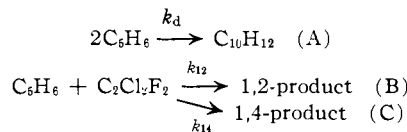
$$R_1 = \frac{x}{y}, R_2 = \frac{1-x}{1-y}; y = \frac{R_2 - 1}{R_2 - R_1}, x = R_1 y$$

The ratio of rate constants,  $k_p/k_H$ , is given by<sup>7</sup>

$$k_p/k_H = \log x / \log y \quad (4)$$

$R_1$  and  $R_2$  were found experimentally to be 0.0916 and 9.90, respectively. The ratio  $k_p/k_H$  based on these values and the above assumptions was 25.

**Estimate of the Rate Constant for Cycloaddition of 1,1-Dichloro-2,2-difluoroethylene to Cyclopentadiene.**—In this case the final product composition is the result of competition for cyclopentadiene between 1,1-dichloro-2,2-difluoroethylene and a second molecule of cyclopentadiene itself.



Let  $k_{12} + k_{14} = k_a$

$x$  = concentration of cyclopentadiene

$y$  = concentration of 1,1-dichloro-2,2-difluoroethylene

Then  $\frac{d(A)}{d[(B) + (C)]} = \frac{k_d x^2}{k_a x y} = \frac{k_d x}{k_a y} \quad (5)$

In the experiment 1122 was the solvent and changed in concentration by only 5%;  $y$  is therefore treated as constant and the following substitutions are made

$$y = S$$

$$(B) + (C) = v$$

$$(A) = \frac{1}{2}(x_0 - x - v)$$

$$2k_d/k_a S = f$$

The differential equation now becomes

$$-dx/dv - 1 = fx$$

which is integrated to

$$v = \frac{1}{f} \ln \frac{fx_0 + 1}{fx + 1}$$

This equation can be solved for  $f$ , the only unknown, by successive approximations.

From the cyclopentadiene experiment described in part I,  $x_0 = 1.96$ ,  $x = 0.51$ ,  $v = 0.41$ , and  $S = 7.9$  yielding  $f = 2.24$  and  $k_d/k_a = 8.8$ . Neglecting any solvent effect on the dimerization of cyclopentadiene, we may use Wassermann's Arrhenius parameters for the gas-phase reaction<sup>8</sup> to calculate  $k_d = 5.5 \times 10^{-6}$  l./mole sec. at 80°, which gives  $k_a = 6.2 \times 10^{-6}$  l./mole sec. From the observed ratio of 1,2- and 1,4-additions we obtain  $k_{12} = 1.1 \times 10^{-6}$  and  $k_{14} = 5.1 \times 10^{-6}$  l./mole sec. These figures are the basis of the relative reactivities assigned to cyclopentadiene in Table III.

## Results and Discussion

Figure 1 shows a typical set of kinetic data plotted for a second-order reaction. Table II summarizes

(7) T. S. Lee in "Technique of Organic Chemistry, Rates and Mechanisms of Reactions," Vol. VIII, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1953, p. 100.

(8) A. Wassermann, *Trans. Faraday Soc.*, **34**, 133 (1938).

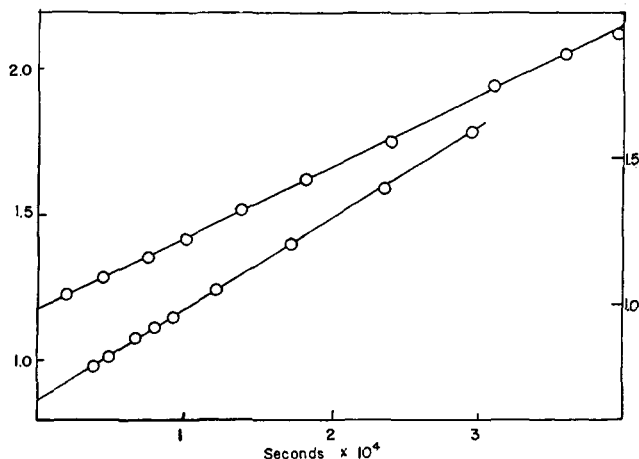


Fig. 1.—Typical rate curves for addition of 1,1-dichloro-2,2-difluoroethylene to butadiene (lower line, left-hand scale) and chloroprene (upper line, right-hand scale). The ordinates are  $\log ((M_t)_0 - M_c)/((M_D)_0 - M_c)$  (eq. 2), based upon v.p.c. areas for the cycloadducts; reaction temperature 81.87°.

the rate constants for a series of dienes and Table III summarizes the relative rates of 1,2-cycloaddition in comparison with the relative rates of the same dienes in reaction with maleic anhydride as reported by Craig<sup>5</sup> and by Sauer.<sup>6</sup> For the 1,2-cycloadditions an individual double bond of butadiene is taken as the standard of reference. For the Diels–Alder reactions butadiene is likewise taken as a standard, but in the former set of measurements the observed rate constant of butadiene is divided by two in order to enable comparison of the addition rates to the nonequivalent double bonds of the substituted dienes.

TABLE II  
KINETIC RESULTS ON CYCLOADDITION OF 1,1-DICHLORO-2,2-DIFLUOROETHYLENE TO DIENES

Diene	Initial concn., M	Temp., °C.	$k \times 10^6$	$k$ rel. to isoprene at same temp
Butadiene	1.288	81.87	$9.02 \pm 0.14$	0.750
	1.262		$9.10 \pm 0.15$	.756
	(By competition)		8.86	.738
Isoprene	1.06	82.00	$12.6 \pm 0.9$	
	0.606		$12.3 \pm .8$	
	.438		$12.0 \pm .5$	(1.0)
	.838	79.5	7.76	(1.0)
Chloroprene	1.007	81.87	$6.69 \pm 0.09$	0.556
	1.028		$6.86 \pm 0.25$	.570
	(By competition)		6.66	.555
<i>cis</i> -Piperylene	0.850	79.5	6.64	.856
<i>trans</i> -Piperylene	0.849	79.5	4.75	.612

The first notable feature of the comparison is that, whereas the methyl group appears to be about equally accelerating in both reactions, the chlorine atom depresses the rate of the Diels–Alder reaction but slightly accelerates the 1,2-cycloaddition. A second striking contrast is seen in the behavior of *cis*- and *trans*-piperylenes. The Diels–Alder reaction of maleic anhydride with *cis*-piperylene is almost undetectably slow under conditions where the *trans* is conveniently measurable. The 1,2-cycloaddition which takes place exclusively at the unsubstituted double bond is accelerated by a factor of 2.3 for *cis*-piperylene but of only 1.65 for the *trans* isomer. Not only is a *cisoid* conformation of the diene system not required, but the *transoid* appears to be slightly more favorable than the *cisoid* for the process of 1,2-cycloaddition. This fact is further illustrated

TABLE III  
RELATIVE RATES OF CYCLOADDITION

Diene	—Cl <sub>2</sub> C=CF <sub>2</sub> —		<i>cis</i>	<i>trans</i>	Maleic anhydride (Diels–Alder reactn.)	
	1,2-	3,4-			Craig 25° <sup>5</sup>	Sauer <sup>6</sup>
	1	1			1	1
	2.3	0.42			2.9	2.25
	1.2	0.30			0.14	0.10
	[0.053]	2.3			Very small	
	[0.028]	1.65			4.8	3.3
	0.113	0.113			1350	
					0.046	
			[0.087]	[0.064]		
			[0.12]			

in the case of cyclopentadiene which, in the Diels–Alder reaction, is 1350 times as reactive as butadiene but, in its total reaction with 1122, is only about 70% as reactive as butadiene.

On the basis of the biradical mechanism for 1,2-cycloaddition, we might expect that the activating influences of a methyl group and of a chlorine atom would be in the same proportion as the ability of these substituents to stabilize a methyl radical. The rates of decomposition of *t*-butyl trimethylperacetate and *t*-butyl trichloroperacetate are both enhanced compared to the perester of unsubstituted acetic acid in a way which indicates that the *t*-butyl and trichloromethyl radicals are being liberated in the rate-determining step.<sup>9</sup> The rate constants for *t*-butyl and trichloromethyl are in the ratio of 3.2:1. The stabilizing effect of a single methyl radical and of a single chlorine atom should be related as the cube root of this number, or 1.5. The rates of 1,2-addition to the substituted double bond in isoprene and chloroprene are in the ratio 1.9. Thus, the ability of a substituent to stabilize a free radical is related to its influence on the rate of 1,2-cycloaddition when that cycloaddition can proceed by way of an intermediate having radical character at the seat of the substitution. The fact that this possibility exists also in the Diels–Alder reaction does not prevent its rate from responding quite differently to substitution (ratio 21).

When the methyl group and the chlorine atom are so located that the intermediate in cycloaddition has no radical character at the position of substitution, both substituents appear to have a depressing effect upon 1,2-cycloaddition. This conclusion is arrived at by tabulating that portion of the isoprene and chloroprene rate constants attributable to 3,4-addition at the unsubstituted double bond. This result suggests that the activating effects of both of these groups on 1,2-cycloaddition are exerted over a general deactivating effect which occurs as a result of the presence of any substituent at the 2-position. Since this effect, like the activating effect, is of the same sign for methyl and chlorine, it cannot be polar in origin but could be due to a deplanarizing tendency which allows the diene system to be less frequently in the most favorable position for attack with formation of an allylic radical.

(9) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1399 (1958).

The competitive experiment described between *cis*-piperylene and *trans-trans*-hexadiene enables us to estimate the effect of nonterminal location of a double bond upon its reactivity in cycloaddition. We conclude that one double bond of *trans-trans*-hexadiene undergoes cycloaddition with 1,1-dichloro-2,2-difluoroethylene 0.046 times as fast as a double bond of butadiene. There is thus a very substantial deactivating effect arising from terminal substitution on a double bond even by a methyl group. If the initial step in 1,2-cycloaddition bears any resemblance to the chain-propagating reaction in free radical polymerization, then this effect is not unexpected, it being well known that only terminal olefins are highly active participants in this reaction.

From the results of part II we know that in *trans-cis*-2,4-hexadiene the rates of cycloaddition to the two double bonds are not equal, there being a slight but definite preference for addition to the *cis* double bond. The bracketed figures in Table II represent an attempt to place these reactivities on a semiquantitative basis. First, we assume that by changing one of the double bonds of *trans-trans*-hexadiene from *trans* to *cis* we are affecting the reactivity of the remaining *trans* double bond in the same ratio as in going from *trans-* to *cis*-piperylene. The relative reactivity assigned to the *trans* double bond of *trans-cis*-hexadiene is then  $0.046 \times 2.3/1.65 = 0.064$ . From the relative total amounts of addition to the two double bonds of *trans-cis*-hexadiene, we then find a relative reactivity of 0.087 for the *cis* double bond. The further assumption that the reactivity of the *cis* double bond is increased by a further factor of 2.3/1.65 gives us an estimated 0.12 for the reactivity of a double bond in *cis-cis*-2,4-hexadiene. This is close to the 0.11 determined for 1,2-cycloaddition to cyclopentadiene, but the significant comparison here

would be with the total rate of 1,2- and 1,4-addition (0.70), which should reflect the rate of formation of the biradical. This rate, without regard to the subsequent branching of the reaction path into 1,2- and 1,4-addition (see part I), may indicate the favoring influence of forced coplanarity compared to the freer rotation, or at least libration, in *cis-cis*-2,4-hexadiene. This requires a nonbiradical element in the Diels-Alder reaction to be responsible for the acceleration of four orders of magnitude relative to the position which cyclopentadiene would otherwise hold.

Finally, if we suppose that the reactivities of the non-terminal double bonds in the piperylenes are related to the corresponding reactivities in the hexadienes as the measured rates in the piperylenes themselves are to that of butadiene, we obtain the bracketed estimates of 0.053 and 0.028 for the relative rates of addition of 1,1-dichloro-2,2-difluoroethylene to the substituted double bonds of *cis-* and *trans*-piperylenes, respectively. This estimate calls for 2.3 and 1.7% of the unfavored product to be found in the cycloadduct. Such amounts if present should be detectable in the absence of special problems of resolution.

We conclude from this kinetic study that 1,2-cycloaddition of 1,1-dichloro-2,2-difluoroethylene and 1,4-cycloaddition of maleic anhydride are governed by entirely different factors. In the former reaction the effect of chlorine substitution in the 2-position and of methyl substitution in the 2- and 4-positions can be fully rationalized in terms of a reaction mechanism involving a biradical intermediate. The special effects due to polar character, blocking of *cisoid* diene conformation, and cyclic character of the diene, all of which are familiar in the Diels-Alder reaction, are absent here.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

## Cleavage Reactions of Tertiary Nitro Anion Radicals

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The chemical and electrochemical reductive behavior in glyme of the representative tertiary nitro compounds 2-nitro-2,4,4-trimethylpentane, 2-phenyl-2-nitropropane, 2,2-dinitropropane, and *t*-nitrobutane has been studied. Polarographic, cyclic voltammetric, and e.s.r. data are used to clarify the gross mechanistic features of the reactions of each nitro compound upon reduction by metallic sodium in glyme. For each compound, reduction leads to an intrinsically unstable anion radical which cleaves to nitrite ion and a corresponding free radical. The subsequent reactions of these free radicals, however, differ among the several nitro compounds. These reaction differences are related to whether the radical can be further reduced to anion under the reaction conditions and also to the lifetime of the parent nitro anion radical.

### Introduction

While numerous stable anion radicals are known,<sup>1-4</sup> the existence of anion radicals which are unstable with respect to their decomposition into anions and radicals has only been postulated. Thus, electroreduction of alkyl halides<sup>5</sup> and the reductive dearylation of aryl phosphates<sup>6</sup> and triphenylphosphine oxide<sup>7a,b</sup> are presumed to proceed *via* cleavage of initially formed

anion radicals into anions and radicals. In an earlier communication<sup>8</sup> we have established that an unstable anion radical results from the reduction of *t*-nitrobutane. This decomposed to form a remarkably stable liquid free radical, di-*t*-butylnitroxide.<sup>9</sup> Subsequent work designed to elucidate the mechanism and scope of this unusual transformation has established that the reductive conversion of nitro compounds to their corresponding nitroxides in substantial yields is not general. The formation of nitroxide in substantial yields is, in fact, specific to *t*-nitrobutane among various nitro compounds studied. For other tertiary nitro compounds, reactions which do not form nitroxides predominate. It is the purpose of this paper to examine the reactions of anion radicals derived from

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