Ene Reactions of Conjugated Dienes. Rate Enhancements in Cyclic 1,3-Dienes and Dependence of Ene Adduct:Diels–Alder Adduct Ratio on Enophile Structure

Barry M. Jacobson,* Adrianne C. Feldstein, and Joan I. Smallwood

Department of Chemistry, Barnard College, New York, New York 10027

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The cis hexalin **1** gives varying proportions of ene and Diels–Alder adducts with a variety of dienophiles. The rate constants for the Diels–Alder reaction with maleic anhydride showed a marked drop in the sequence isoprene, 1,3-cyclohexadiene, **1**, but the ene reaction rate constant with diethyl azodicarboxylate showed a marked increase in the same series. For **1** the percentage of ene adduct increased with a more highly substituted enophile/dienophile. Azo dienophiles gave more ene adduct than the correspondingly substituted carbo dienophile. Although the first trend is loosely consistent with a differential steric effect for the two reactions, the results with some enophiles do not fit such an explanation well. It is concluded that acceleration of the ene process, not just hindrance of the Diels–Alder, is responsible for the formation of ene adducts in some cases. Stereoelectronic factors are proposed as being of primary significance, ahead of steric ones.

Although the Alder ene reaction[1] is quite common with simple alkenes,[2] it occurs relatively infrequently with conjugated dienes because most good enophiles are also effective Diels–Alder dienophiles. Ene reactions are seen with highly hindered dienes which cannot achieve the syn arrangement required for the Diels–Alder reaction[3] and with a few cyclic dienes and trienes, particularly when azodicarboxylate esters are the reaction partners or when the diene is a steroidal system that is simply too crowded to allow for a Diels–Alder reaction.[4] Gillis has suggested[3a,5] that the trans arrangement of the azo esters, combined with some hindrance from ethano or larger bridges, suffices to explain the appearance of the ene products observed with cyclic dienes, although the ene reaction appears to be subject to steric hindrance also,[6] probably because of the preferred orbital geometry[7] for the concerted hydrogen migration.[8]

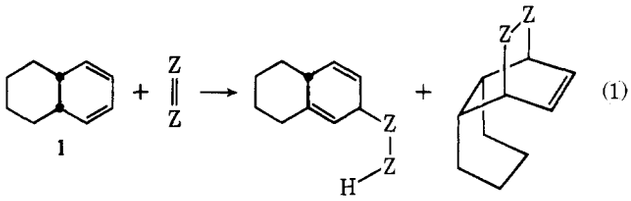
However, in discussions of these reactions[3-5] the implicit assumption seems to have been made that an ene reaction with a 1,3-diene makes its appearance solely because the Diels–Alder reaction has been blocked; i.e., the ene reaction is merely unmasked and in the absence of steric hindrance could not compete successfully. Indeed, rarely do both ene and Diels–Alder products appear simultaneously,[9] but no test directly addressing the matter of this supposed unmasking seems to have been made.

Conversely, since a single substrate diene which consistently affords both ene and Diels–Alder products has not been available, there seems also to have been no direct comparison between the enophilic and dienophilic behavior of the reacting partner. It has been noted that *trans*-diethyl azodicarboxylate (DEAD) has greater enophilic reactivity than its cis isomer[5] or than 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD),[5,10] while dienophilic character runs oppositely,[5,11] but otherwise no general characterizations with respect to enophile constitution have been made.

We report here some evidence that enhanced reactivity in the ene reaction rather than (or at least in addition to) decreased reactivity in the Diels–Alder reaction is responsible for the appearance of ene products with cyclic 1,3-dienes. Furthermore, the trend to lower ene reactivity with increasing substitution[6] (and thus presumably steric hindrance) in simple alkenes is reversed in some cases as well. Finally, one of the compounds used in this study does behave as a fair diene for the Diels–Alder reaction while being highly reactive in an ene fashion. This allowed for some exploration of the factors influencing enophilic vs. dienophilic behavior in a single system.

Results and Discussion

Compound **1**, *cis*-1,2,3,4,4a,8a-hexahydronaphthalene, was previously found to undergo appreciable ene reaction in competition with a Diels–Alder process using any of a number of dienophiles[12,13] (eq 1). Of itself, this was unremarkable,



1 (1)

since **1** may simply be regarded as a more hindered version of 1,3-cyclohexadiene. The latter reacts in similar fashion with azodicarboxylate esters.[3a,4b,c] We have measured the second-order rates for the reaction of **1** with maleic anhydride, yielding 98% Diels–Alder adduct, and with diethyl azodicarboxylate (DEAD), yielding an ene adduct exclusively. Table I gives the values of the rate constants as well as those for the same pair of reagents reacting with 1,3-cyclohexadiene and with isoprene. The 1,3-cyclohexadiene gives only a Diels–Alder product with maleic anhydride[14] and mostly ene product with DEAD.[3a,4b,c] Isoprene yields only Diels–Alder adducts with both reagents.[15,16] The rate constant for the reaction of isoprene with DEAD has not previously been published. The latter reaction was found to be cleanly second order, though at very high isoprene concentrations some curvature of the second-order plots could be seen.

While the rate constants for the reactions with maleic anhydride do show the expected decline, the rate constants for reaction with DEAD increase markedly. Thus, although **1** must surely be more crowded than 1,3-cyclohexadiene and indeed gives a much slower reaction with maleic anhydride, it reacts some 14 times faster with DEAD. The comparison with isoprene is perhaps somewhat uncertain, since the latter gives only Diels–Alder products, but the very absence of an ene component indicates again a large rate difference; the total rates for reaction of DEAD with both 1,3-cyclohexadiene and isoprene are similar so that any ene reaction with isoprene must have a much smaller rate constant. Thus, the decrease in the rate of the Diels–Alder reaction is not the sole cause for appearance of an ene product.

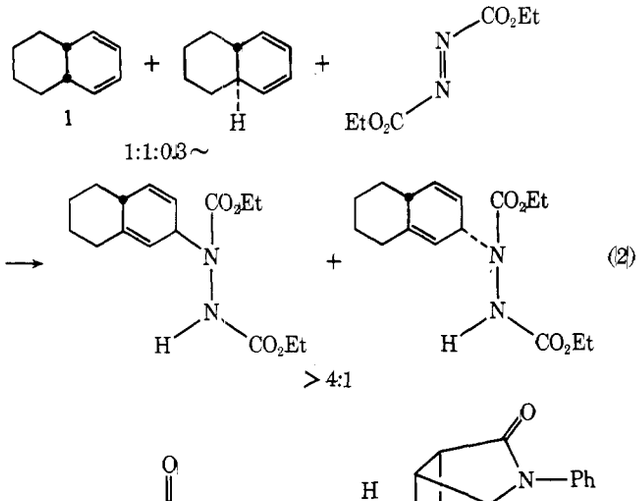
These results do not at all imply that steric hindrance actually accelerates the ene reaction. A simple competition was run between **1** and its trans isomer, **10**, for DEAD and for

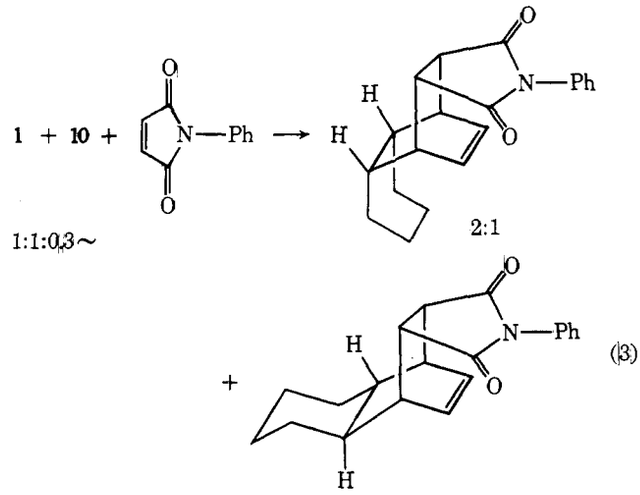
Table I. Rate Constants for Diels–Alder and Ene Reactions

Diene	Rate constant with maleic anhydride,[a] $\times 10^7$ L mol^{-1} s^{-1}	Source	Rate constant with DEAD[b] $\times 10^7$ L mol^{-1} s^{-1}	Source
Isoprene	1540	*c*	670[d]	This work
1,3-Cyclohexadiene	1320	*c*	760	*e*
1	8.7	This work	11 500	This work

[a] In dioxane at 30 °C. [b] In cyclohexane at 25 °C. [c] Reference 17. [d] Diels–Alder product only, no ene product detected. [e] Reference 20.

N-phenylmaleimide (eq 2 and 3). Compound **10**, like **1**, gives only ene product with DEAD and greater than 95% Diels–Alder product with *N*-phenylmaleimide, but **1** is at least ten times more reactive toward DEAD (at room temperature; it is four times more reactive at 150 °C) and two times more reactive toward the imide (at 150 °C). This result was at first somewhat surprising; **10** has a statistical advantage over **1** (in the ene reaction), since it has both its allylic hydrogens in the axial position and thus in the preferred parallel alignment to the diene's π orbitals. However, examination of models showed that if the dienophile or enophile extended out over the second ring, there would be more steric repulsion to both reagents upon approach to *either* face of **10**. *cis*-**1** has greater hindrance on the side lacking the allylic hydrogens, but far less on the other, reactive face (see Figure 1).





To explain all these results, it would appear that a stereoelectronic factor is at least as important as pure steric

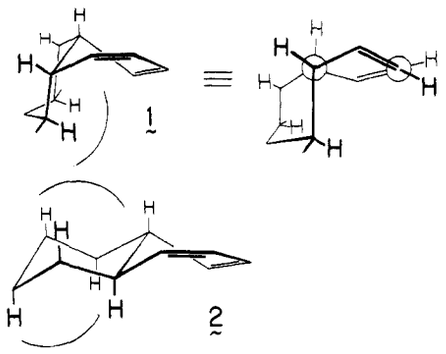


Figure 1.

hindrance. In all the cyclic dienes, both here and in earlier work, at least one abstractable hydrogen is held in rough alignment with the π system and rotation away from this favored alignment is either slow or impossible. No such limit to rotation applies, in general, to the acyclic alkenes and dienes.[18] Unfortunately, simple cyclic alkenes, the compounds that could be used most easily to test the generality of this stereoelectronic effect, react with azo esters through a free-radical mechanism[19] and rate constants do not seem to be available for other enophiles. It may be noteworthy, however, that 1,4-cyclohexadiene reacts a good deal more rapidly with DEAD than do the simple alkenes.[6,20]

It may also be noted that the abstracted hydrogens in **1** and **10** are tertiary, that removed in the cyclohexadienes is secondary, and the hydrogen that would have to be abstracted in isoprene is primary. In their work with simple alkenes, Thaler and Franzus claimed that the primary, secondary, or tertiary character of the hydrogen was irrelevant.[6] However, since all the compounds involved except 1,4-cyclohexadiene were acyclic, any such effect could have been compensated for by the steric differences previously mentioned, and dependence on bond strength or on other characteristics paralleling the primary, secondary, or tertiary nature of the hydrogens might be observable only with cyclic or other relatively rigid compounds. Of course, it may be the fact that it is a *diene* reacting which has introduced a dependence of the rate on the type of hydrogen abstracted. In this connection, it should be noted that the rate constants for **1**, **10**, and 1,3-cyclohexadiene are also all significantly greater than that for 1,4-cyclohexadiene. It remains to be seen if acyclic dienes will show any such dependence or rate accelerations. Synthesis of an appropriate set is underway.

Since **1** does give both Diels–Alder and ene adducts simultaneously, it served as a "standard" substrate for a number of dienophiles in a survey of the competition between the two processes. The dienophiles used are listed in Chart I. Reactions were run in *N*,*N*-dimethylacetamide, generally at 165 °C with the solutions being degassed and sealed in ampules.

Chart I. Dienophiles Used

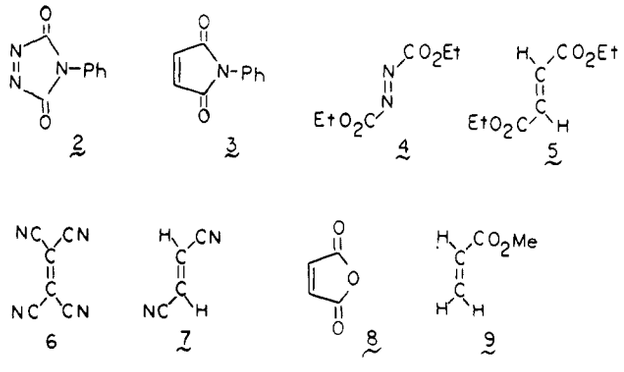
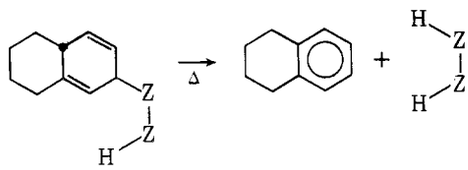


Table II. Ene and Diels–Alder Adducts from Reaction of 1

Registry no.	Dienophile	Diels–Alder: ene adduct ratio	Temp, °C	Material balance,[a] %
4233-33-4	2	90:10[b,c]	25	99
	2	75:24[b,c]	164	99
941-69-5	3	97.7:2.3[c]	165	89
4143-61-7	4	0:100[b,c]	60	97
	4	0:100[b,c]	165	96
623-91-6	5	80:20[d]	165	98
670-54-2	6	40:60[c]	60[e]	87
764-42-1	7	79:21[d]	165	101
108-31-6	8	97.7:2.3[d]	165	99
96-33-3	9	45:55[d]	165	75

[a] Sum of Diels–Alder and surviving ene adduct, tetralin from ene adduct that had decomposed, and recovered diene. Dienophile usually used in excess. [b] Determined by NMR. [c] Determined by NMR (Diels–Alder) and by VPC (yield of tetralin). [d] Determined by NMR (Diels–Alder and undecomposed portion of ene adduct) and VPC (tetralin from decomposed ene adduct). [e] Appreciable charring at higher temperatures with lower material balance.

Exceptions were the reaction with PTAD (2), which reacted too rapidly for an ampule to be prepared, and tetracyanoethylene (6), which gave charring above 60 °C. In all cases, both Diels–Alder and ene adducts were isolated and characterized in separate additional runs, though the latter were usually conducted at lower temperatures to ensure the preservation of the less stable ene adducts (vide infra). The ratios of ene to Diels–Alder adducts were obtained from absolute yields (measured against added internal standards). The yields of all Diels–Alder products and of stable ene products were determined by NMR. Without exception, the Diels–Alder adducts showed their alkene resonances between δ 6.1 and 6.5. The ene adducts contrastingly came between δ 5.1 and 6.0, and of course gave larger integrals relative to the upfield signals. Partial or complete decomposition of the ene adduct under the reaction conditions occurred with several enophiles (eq 4) but, as the decomposition in every case cleanly yielded



(4)

tetralin, determination of the latter by VPC allowed the original ene product yield to be measured. In fact, it was frequently convenient to pyrolyze the initial products, converting all the ene adduct to tetralin. The Diels–Alder adducts and starting diene were found to be thermally stable under the pyrolysis conditions (180–200 °C, sealed degassed ampules). Although the decomposition of the ene adducts was specifically shown to be quantitative in only a few cases,[21] when both the NMR and VPC methods could be applied the yields generally agreed to within 1–2%. Determination of recovered diene as well as adducts gave a high material balance in almost all cases as further assurance that the product ratios measured were meaningful.

The proportions of Diels–Alder vs. ene adduct are shown in Table II. Certain items stand out. Azo dienophiles give more ene reaction than the corresponding carbo dienophiles (compare results using 2 with those using *N*-phenylmaleimide (3) and then diethyl azodicarboxylate (4) with diethyl fumarate (5)). Trans substitution in the dienophile yields more ene adduct than cis, and tetrasubstitution apparently even more.[22] Although this trend may well be the result of steric crowding and hence preferential suppression of the Diels–Alder reaction, such an argument is subject to some criticism. First, the result with methyl acrylate (9) is clearly anomalous, even given the limited material balance in this case. Second, diethyl fumarate and fumaronitrile (7) give very similar product ratios, although one might expect the carbethoxyl group to show a greater steric effect.[23] Third, the absolute rates of all the reactions vary enormously, from essentially as fast as mixing (for PTAD (2) even at room temperature) to having a half-life of over 2 days (for 7 and 9), and there is no relationship between these rates and the percentage of ene adduct. In view of this rate difference, any steric effect is being superimposed on a very much larger electronic one, with the latter affecting both ene and Diels–Alder reactions in *almost* identical fashion. Thus, many of the apparent steric effects may be no more than a coincidental pattern: the result of some very slight electronic difference between cis and trans dienophiles, for example. Perhaps a secondary orbital interaction[26] between a π-electron-containing substituent on the enophile and the other double bond of the diene or a slight difference in orbital energies of the cis and trans enophiles[27] is what tips the balance between Diels–Alder and ene pathways. In the hope that substitution of the dienophile with non-π-electron-containing substituents might throw some light on this, reaction of 1 was attempted with ethyl crotonate (for comparison to the fumarate). However, there was negligible reaction of any kind at 170 °C even after several days, and at 210 °C the decomposition of the diene to undetermined products became the predominant process. This matter remains to be explored.

Experimental Section

Capillary melting points (uncorrected) were taken on a Thomas-Hoover melting-point apparatus. NMR spectra were obtained using a Varian T-60 instrument. IR data were from a Perkin-Elmer 710A or Beckman IR-5. Analyses were done by Galbraith Laboratories, Knoxville, Tenn.

Materials and Purification Procedures. Dienes 1 and 10 were prepared as in earlier work[13] and purified by preparative VPC (20% Carbowax 20M on Chromosorb P) before use. Isoprene (Eastman white label) was distilled and stored under refrigeration. Cyclohexane (Fisher Spectrograde) was used as received. Maleic anhydride (Eastman white label) was resublimed before use. *p*-Dioxane (Fisher) was dried and partially purified by passage through grade I basic alumina, stirred overnight with $LiAlH_4$, and distilled from the $LiAlH_4$ under N_2. 4-Phenyl-1,2,4-triazoline-3,5-dione was prepared according to the literature,[28] and resublimed before use. Diethyl fumarate (Eastman white label) and methyl acrylate (Aldrich) were used as received. Tetracyanoethylene (Aldrich) was sublimed before use. Fumaronitrile and *N*-phenylmaleimide were prepared by literature procedures.[29] Decane was used as received (Aldrich) after VPC showed a single peak. *m*-Dinitrobenzene was prepared by nitration of nitrobenzene and recrystallized twice from 95% ethanol. *N,N*-Dimethylacetamide was prepared by treatment of acetic anhydride with 40% dimethylamine, distillation, removal of the acetic acid in the azeotrope by stirring with a saturated solution of $NaHCO_3$, extraction of the amide into benzene, and redistillation on a 3-ft column of glass helices. A cut boiling from 163–164 °C was used. Ethyl crotonate was prepared by Fischer esterification of crotonic acid (Eastman White Label).

Kinetics, 1 and Diethyl Azodicarboxylate. The rates were high enough to permit direct measurements of the DEAD concentration by UV without dilution of the sample. The diene was weighed into a 5-mL volumetric flask partially filled with cyclohexane from which the oxygen had been removed by entrainment with nitrogen. The DEAD was weighed in and the flask transferred to a bath at 25.0 °C, swirled 1 min, and filled to the mark. A UV cell was immediately filled with this solution and placed in the thermostated cavity of a Beckman DB-G spectrometer. Initial diene concentrations were varied by a factor of 10 and initial DEAD concentrations by a factor of 3. All runs were done in duplicate. Data were plotted by standard methods[30] and rate constants calculated by a least-squares fit. *R* values for all runs were >0.99. One set of runs in which no attempt was made to exclude atmospheric oxygen gave the same rate constant within 10%, values being scattered among the oxygen-free numbers.

Isoprene and DEAD. The same procedure as above was followed for runs at low DEAD concentration, but for a reasonable rate when

the isoprene concentration was reduced the initial DEAD concentration needed became too high for direct measurement in the reaction mixture. In these cases, the reaction was run in a 25-mL volumetric flask; aliquots were removed periodically, diluted, and checked by UV. Initial concentrations of the reactants were varied by factors of 6 (DEAD) and 13 (isoprene).

1 and Maleic Anhydride. Diene, maleic anhydride, and 1,3-dinitrobenzene (as in internal standard for integration) were weighed into a 1-mL volumetric flask, the flask placed in a bath at 30 °C, and purified dioxane added to the mark. The solution was transferred to a jointed NMR tube, degassed by freeze–pump–thaw sequences, and sealed. The tube was immersed in a bath held at 30 °C and monitored periodically by NMR. (At the concentrations and temperature used the half-lives were generally 24 h or more, so that sample preparation time and measurement times introduced a negligible error.) Initial concentrations of diene were varied from 0.5 to 1.0 M, those of maleic anhydride from 0.6 to 3.0 M; greater variation was precluded by the low rate of reaction and limited sensitivity of the NMR method.

Competition between 1 and 10 for DEAD or *N*-Phenylmaleimide. Decane was used as an internal VPC integration standard; FID relative responses for **1**:**10**:decane were 1.00:1.00:1.09. For a typical run, a solution equimolar in **1** and **10** in dimethylacetamide with a weighed amount of *n*-decane was prepared. One-third of an equivalent of DEAD or *N*-phenylmaleimide was added and the solution was sealed in vacuo after degassing by freeze–pump–thaw cycling. After reaction was complete (overnight at room temperature or 1 h at 150 °C for DEAD, overnight at 150 °C for the imide), the tube was opened and all volatiles were distilled trap-to-trap at 0.01 mm. Ratios of unreacted starting dienes vs. decane were determined by VPC on a 10 ft × ⅛ in. 10% Carbowax 20M column (Chromosorb W) using a Varian Model 1200 Chromatograph equipped with a Linear Instruments Model 252A electronic integrating recorder. At the relatively high ratios of dienophile to diene used, competition ratios are obviously only an approximation to rate-constant ratios, but at lower concentrations the amount of diene reacted becomes too small for precise measurements and the ene products with DEAD are thermally unstable; adducts from *both* dienes yield tetralin and *sym*-diethyl hydrazinedicarboxylate on heating or passage through the VPC, so that determination of competition ratios by product analysis is not possible.

Reactions of 1 with Dienophiles 3–9; General Procedure. A stock solution of **1** (0.681 g) and decane (0.445 g) in *N,N*-dimethylacetamide (total volume 10 mL) was prepared and 1-mL aliquots were pipetted into jointed test tubes. A 5–10% molar excess of dienophile was weighed into the tube which then was immediately immersed in a dry ice bath. Each tube was degassed by repeated freeze–pump–thaw sequences and sealed. The tubes were then immersed in a stirred oil bath held at 165 ± 3 °C for varying lengths of time (5 min for DEAD and TCNE; overnight for maleic anhydride, diethyl fumarate, and *N*-phenylmaleimide; and 3–4 days for fumaronitrile and methyl acrylate). Reactions with DEAD were also heated for longer times on occasion at 180–200 °C when complete decomposition of the ene adduct was desired. The tubes were then cooled and opened, their contents were washed into a small flask with more dimethylacetamide, and the solutions distilled trap-to-trap (30 °C at 10^{-2} mm). The distillates were examined by VPC (10 ft × ⅛ in. Carbowax 20M on 60/80 acid-washed Chromosorb W, temperature programmed 6 °C/min from 50 to 180 °C). VPC traces were recorded on a Linear Instruments Model 252A recorder equipped with an electronic integrator. All samples were injected in triplicate. The FID response factors for the diene **1** and tetralin relative to decane were measured earlier (0.91 for the diene, 0.90 for tetralin). The residue from the distillation was completely dissolved in a minimum volume of $CDCl_3$ after addition of a weighed amount of *m*-dinitrobenzene (used as an NMR integration standard, since its signals fell below all of those from the reaction products) and examined by NMR. Reactions with TCNE and DEAD as dienophiles were also carried out at 60 °C, with the former to prevent charring and the latter to preserve the ene adduct.

Reaction of 1 with PTAD (2). An aliquot of the diene–decane solution was heated to 165 °C and a solution of PTAD in dimethylacetamide was added dropwise until the red color remained more than a second. The solution was then treated as with the other dienophiles. Two samples were transferred to jointed test tubes, degassed, sealed, and heated at 180–200 °C for several hours to decompose the ene adduct.

Isolation and Characterization of Products.[31] Ene Adduct of TCNE and 1. Freshly sublimed TCNE (0.65 g) and a slight excess of **1** (0.70 g) were placed in a jointed test tube in 3 mL of tetrahydrofuran (distilled from $LiAlH_4$). The tube was cooled in dry ice, evacuated to 10 mm pressure by a water aspirator, and sealed. The tube was placed in a freezer at −10 °C until the purple color of the solution had faded to yellow. The tube was opened and its contents were poured into ice-cold 10% NaOH. The mixture was shaken well and the aqueous layer then extracted twice with portions of ether. The pH of the aqueous layer was then adjusted to approximately 3 with cold 2 M HCl and the precipitated ene adduct immediately collected, rinsed with ice-water, and dried under a vacuum desiccator in a refrigerator. This procedure removes the bulk of the Diels–Alder adduct, but complete purification is not possible. The ene adduct is moderately stable in solid form but solutions decompose rapidly, especially if the solvent is polar or heated. The adduct does not survive chromatography of any sort. Low-temperature crystallization from ether is possible but also fails to purify it completely. Acetone or ethanol solutions decompose in a few hours to give tetralin and tetracyanoethane, both of which were isolated and compared to authentic samples: Adduct NMR (acetone-d_6) δ 1–2.0 (m, 6 H), δ 2.2–2.5 (m, 2 H), δ 2.8 (m, 1 H), δ 3.8 (m, 1 H), δ 5.5–6.1 (m, 4 H).

Diels–Alder Adduct of *N*-Phenylmaleimide and 1. *N*-Phenylmaleimide (120 mg) and diene **1** (70 mg) were dissolved in 1 mL of *o*-dichlorobenzene in a jointed test tube, the tube was cooled, the air pumped out, and the tube sealed. The sample was heated overnight at 130 °C. On opening, most of the *o*-dichlorobenzene was evaporated under a stream of N_2 and the residue chromatographed on 20 g of silica gel (10:1 petroleum ether/ether eluent). The product (75 mg) was recrystallized from 95% ethanol to give white crystals: mp 204–205.5 °C; NMR ($CDCl_3$) δ 1–2.0 (m, 10 H), δ 3.05 (m, 4 H), δ 6.23 (d of d, J = 3, 4 Hz, 2 H). There was no evidence that more than one isomer was present, though a second isomer cannot be ruled out.[12] Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 77.50; H, 6.98; N, 4.52.

Products from Methyl Acrylate and 1. Diene **1** (0.5 g, 3.7 mmol) and methyl acrylate (0.5 g, 5.8 mmol) were degassed and sealed in a jointed test tube and heated at 165 °C for 4 days. The tube was cooled and opened and the colorless liquid distilled (molecular still) at 0.01 mm to free the adducts from polymeric material. The distillate was then injected 50 μL at a time through a 6 ft × ¼ in. 20% Carbowax column at 190 °C. Three slightly overlapping peaks were collected but only the last (a Diels–Alder product) could be obtained completely pure. The first peak appeared to be a Diels–Alder product: NMR (CCl_4) δ 0.8–2.7 (m, 15 H), δ 3.60 (s, 3 H), δ 6.1 (m, 2 H). The second peak was the ene adduct: NMR (CCl_4) δ 1.0 (d, J = 7 Hz, 3 H), δ 1.0–2.8 (m, 10 H), δ 3.2 (m, 1 H), δ 3.65 (s, 3 H), δ 5.2–5.6 (m, 3 H). The third peak had: NMR (CCl_4) δ 1.0–2.0 (m, 12 H), δ 2.2–2.8 (m, 3 H), δ 3.60 (s, 3 H), δ 6.05 (m, 2 H). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.47; H, 9.12. The isolated first two peaks did not give satisfactory analyses; however, a sample of the distilled but not VPC'd material did, so that it appears partial decomposition on the column of either the first Diels–Alder product, or, more likely, the ene product, was occurring.

Products from Fumaronitrile and 1. Diene **1** (0.5 g, 3.7 mmol) and fumaronitrile (0.5 g, 6.4 mmol) were degassed and sealed in a tube which was then heated to 165 °C for 4 days. After cooling and opening, the tube's dark-brown contents were chromatographed on Florisil (5:1 hexane/ethyl acetate eluant) to yield brown oily crystals. The crude product was sublimed at 0.02 mm to yield 0.2 g of light-yellow sticky crystals. These were dissolved in 1 mL of hot ethanol and 3 mL of 1 M KOH in ethanol was added and the solution refluxed for 2 days. The ethanol was evaporated and the residue dissolved in water. Acidification yielded a white solid. The NMR of the solid was virtually identical to that yielded by hydrolysis of a mixture of the crude adducts of diethyl fumarate and diene **1** (also a 80:20 mixture of Diels–Alder and ene adducts).

Product from DEAD and 1. **1** (0.3 g, 2.2 mmol) and DEAD (0.32 g, 1.8 mmol) were mixed in a few milliliters of solvent (benzene, cyclohexane, or dimethylacetamide) from which oxygen had been removed by entrainment with nitrogen. The solution was allowed to sit under nitrogen until the yellow color of the dienophile faded to colorless (overnight). The solvent was evaporated without heating. The residue was recrystallized by dissolving in a 1:1 mixture of ether and petroleum ether at room temperature and then cooling to −30 or −40 °C. Alternatively, the product may be chromatographed on Florisil using an elutant of 3:1 petroleum ether/ether. If the latter method is used, it is important that an excess of diene be present in the original reaction because any unreacted DEAD will decompose on the column and contaminate the product. The white crystalline ene product melts at 103.5–105 °C: IR (CCl_4) 3400, 3030, 2980, 2940, 2860, 1760, and 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (two overlapping t, J = 8 Hz, 6 H), δ 1.2–2.5 (m, 9 H), δ 4.15 (two overlapping q, J = 8 Hz, 4 H), δ 5.2–6.0 (m, 4 H), δ 6.25 (br s, 1 H). Anal. Calcd for $C_{16}H_{24}N_2O_4$: C, 62.32; H, 7.84; N, 9.08. Found: C, 62.50; H, 7.86; N, 9.06. Upon heating to 170

°C for a few hours in a sealed degassed tube, a quantitative yield of tetralin and *sym*-diethyl hydrazinedicarboxylate was isolated.

Product from Maleic Anhydride and 1. (Product isolated as the diacid) 120 mg of maleic anhydride and 70 mg of 1 were dissolved in 1 mL of purified dioxane in a jointed test tube. The tube was degassed and sealed and heated in an oil bath at 100 °C overnight. The tube was cooled and opened, and its contents were poured into 5 mL of 95% ethanol containing excess KOH. The solution was refluxed for 0.5 h, cooled, poured into 25 mL of H_2O, extracted with ether, and then acidified with concentrated HCl. An oil separated which crystallized on trituration with petroleum ether. Recrystallization from 95% ethanol yielded white crystals: mp 175–177 °C; NMR ($CDCl_3$) δ 1.0–2.1 (m, 10 H), δ 2.8 (m, 2 H), δ 3.1 (m, 2 H), δ 6.25 (d of d, J = 4 Hz, J = 3 Hz, 2 H), δ 10.2 (br, 2 H). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.60; H, 6.57.

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Registry No.—**1**, 13304-05-7; **1–3** Diels–Alder adduct, 62707-86-2; **1–3** ene adduct, 62707-87-3; **1–4** ene adduct, 62707-88-4; **1–6** ene adduct, 62707-89-5; **1–6** Diels–Alder adduct, 41181-97-9; **1–7** Diels–Alder adduct, 62707-90-8; **1–7** ene adduct, 62707-91-9; **1–8** ene adduct, 62707-92-0; **1–8** Diels–Alder adduct, 62707-93-1; **1–9** Diels–Alder adduct, 62707-94-2; **1–9** ene adduct, 62707-95-3; **10**, 7360-96-5.

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(16) (a) P. Baranger and J. Levisalles, *Bull. Soc. Chim. Fr.*, 704 (1957). (b) Isoprene was chosen for convenience and because its rate constant for reaction with maleic anhydride is close to that of 1,3-cyclohexadiene's[17].
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(18) (a) A referee has pointed out that all conformations of an acyclic diene such as isoprene should have one of the methyl's hydrogens parallel or nearly so to the π system at all times. The point is well taken, but the methyl group should certainly be undergoing far greater libration as well as rotation than **1**, or 1,3-cyclohexadiene, since the barrier to rotation (V_3) is so much smaller than the barrier for ring flipping. Whether or how such motions would affect the ene or other reactions is an intriguing question but very much unexplored territory. It should also be noted that Nickon and coworkers found the same preference for abstraction of an axial endocyclic hydrogen over that of a methyl hydrogen in some photooxygenations,[18b] but the latter may not be a true ene reaction. (b) A. Nickon, J. B. DiGiorgio, and P. J. L. Daniels, *J. Org. Chem.*, **38**, 533 (1973).
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(21) In most cases the isolation of ene adduct of known purity was difficult because of either very low yields or limited adduct stability. The varied mechanisms of the decomposition of the ene adducts will be the subject of a later paper.
(22) It is conceivable, but only in one case (with DEAD where no Diels–Alder adduct was observed), that the Diels–Alder/ene ratio was determined by thermodynamic rather than kinetic control; the Diels–Alder reaction could have been reversible under the reaction conditions, while the ene reaction was not. But with all the other dienophiles, prolonged heating produced no increase in the amount of ene or ene plus ene-derived product nor decrease in Diels–Alder product, even when the ene product broke down to give tetralin. Kinetic control is thus substantiated.
(23) For example, compare the stability of axial vs. equatorial cyano and carbethoxyl groups in cyclohexane. The ΔG value for the former has been measured as 0.15–0.25 kcal/mol,[24] while that for the latter is 1.0–1.2 kcal/mol.[25]
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Two-Bond Carbon–Proton Couplings in 1,2,3,4,5,7,7-Heptachloronorbornene

Anne H. Cain and John D. Roberts*

Contribution No. 5522 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125

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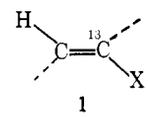
The coupling constants of the carbon–proton and proton–proton bonds were determined for *endo*-1,2,3,4,5,7,7-heptachloronorbornene. Signs were determined for most of the couplings. Comparisons of the norbornene couplings were made with those found in chloroethene and chlorocyclopropane.

Research with a variety of compounds[2] has shown large differences between the two-bond carbon–hydrogen couplings of the type **1** and **2**, and, in fact, with halogenated ethenes,[3] such couplings showed unexpected positive and negative



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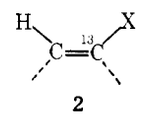

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