°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].
(17) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem., Int. Ed. Engl.*, **1**, 268 (1962).
(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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(31) Certain products have been characterized previously:[13] all products with PTAD, all products with diethyl fumarate, and the Diels–Alder product with TCNE.

Two-Bond Carbon–Proton Couplings in 1,2,3,4,5,7,7-Heptachloronorbornene

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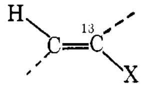
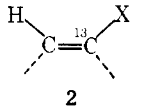
The coupling constants of the carbon–proton and proton–proton bonds were determined for *endo*-1,2,3,4,5,7,7-heptachloronorbornene. Signs were determined for most of the couplings. Comparisons of the norbornene couplings were made with those found in chloroethene and chlorocyclopropane.



1



2

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

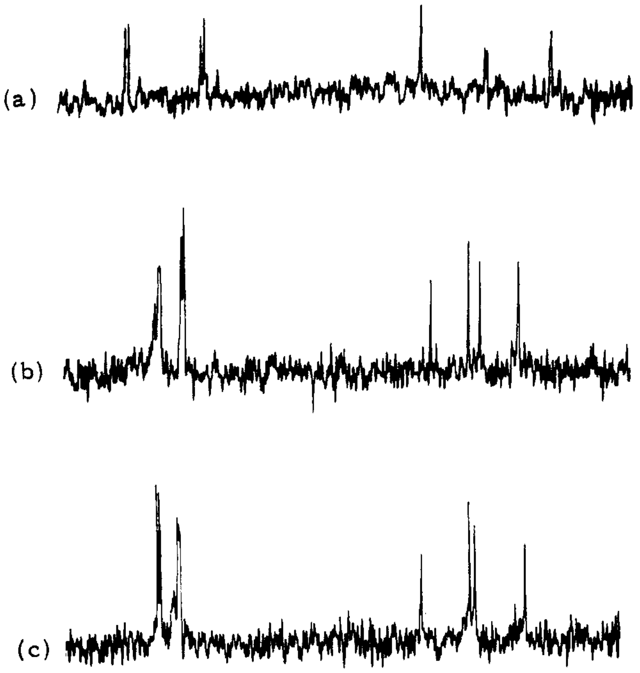
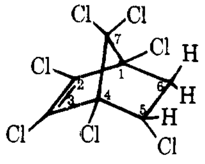


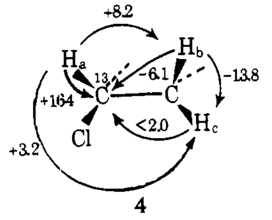
Figure 1. (a) Coupled spectrum of high-field carbons of **4**. (b) and (c) Selectively decoupled spectra of high-field carbons: (b) decoupler set at high-field ^{13}C satellite, and (c) decoupler set at low-field ^{13}C satellite.

couplings. In hope of determining whether positive and negative couplings such as **1** and **2** might be observed more generally than for alkenes we have investigated the couplings in *endo*-1,2,3,4,5,7,7-heptachloronorbornene (**3**).



endo-1,2,3,4,5,7,7-heptachloronorbornene (**3**)

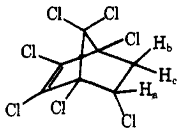
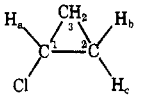
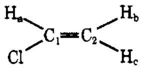
The proton-coupled ^{13}C spectrum of **3** is shown in Figure 1a. From this spectrum and the proton spectrum, the proton–proton and carbon–proton couplings were assigned as in **4**. The proton–proton couplings were assigned by analogy with related compounds. With the usual assumption that vicinal couplings are positive,[4] $J_{H_aH_b}$ was given a positive sign. Independent determinations by Cox and Smith[5] and by Williamson[6] strongly suggest a negative sign for $J_{H_bH_c}$. Selective decoupling of the ^{13}C satellites of H_a, the low-field proton, gave the spectra shown in Figures 1b and 1c. These spectra show that the sign of $^2J_{CH_b}$ is opposite to that of $J_{H_aH_b}$, and $^2J_{CH_b}$ is therefore taken to be negative.



4

The two-bond carbon–hydrogen couplings in **3** are compared with analogous two-bond couplings in Table I. The coupling of $^2J_{CH_b}$ of **3** is similar in magnitude to the trans carbon–hydrogen coupling in monosubstituted ethenes, but is of opposite sign. The cis coupling is much smaller in **3** than in substituted ethenes.

Table I. Two-Bond Carbon–Hydrogen Couplings

Compd and coupling examined		Coupling,[a] Hz	Ref
	$^2J_{CH_b}$ (trans) $^2J_{CH_c}$ (cis)	−6.1 <2.0	This paper
	$^2J_{C_1H_b}$ (trans) $^2J_{C_1H_c}$ (cis)	−1.15 −5.05	2
	$^2J_{CH_b}$ (trans) $^2J_{CH_c}$ (cis)	+7.1 −8.3	3

[a] Positive and negative signs have been included where they are known.

Comparison of the couplings in chloroethenes, heptachloronorbornene (**3**), and chlorocyclopropane is interesting, although some care must be taken when discussing couplings in cyclopropane rings because one could question whether the observed couplings are actually the result of two-bond or three-bond interactions; in general three-bond proton–carbon couplings are larger than corresponding two-bond couplings. Ignoring this problem, the coupling $^2J_{CH_b}$ is negative in both **3** and chlorocyclopropane, as is the case for $^2J_{CH}$ in alkanes and cycloalkanes. There seems to be a general progression of $^2J_{CH_b}$ in these compounds from large positive values in chloroethenes to large negative values in **3**, with $^2J_{CH_b}$ for chlorocyclopropane being intermediate. There is a corresponding change in $^2J_{CH_c}$ which becomes more positive through the series, and was too small to measure for **3**. Why these changes occur is by no means clear. The difference in sign for $^2J_{CH_b}$ and $^2J_{CH_c}$ has been rationalized by Jameson and Damasco[7] but it is not obvious how the argument should be extended to **3** and chlorocyclopropane. It will be interesting to determine whether similar trends in $^2J_{CH}$ will be observed with other series of substances.

Experimental Section

All of the NMR spectra were taken of 0.53 M solutions in $CDCl_3$ referenced to Me_4Si. Proton spectra were obtained with a Varian A-60A NMR spectrometer or on a Varian HR-220 NMR spectrometer. Carbon-13 spectra were taken on a Bruker WH-180 NMR spectrometer using the deuterium in the solvent as a field-frequency lock. The theoretical spectra were calculated using the computer program LEQUOR.

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Registry No.—**3**, 2440-02-0.

References and Notes

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