liner of a steel, high-pressure bomb. After introduction of oxygen, the bomb was warmed, with suitable protection from possible explosions, to 50–55° for 24 hr. and then allowed to cool to room temperature before slowly releasing the oxygen. The solution was evaporated down to a residual oil. This was dissolved in 20 ml. of anhydrous ether and reduced with excess lithium aluminum hydride at room temperature. After addition of water, the ether layer was dried and evaporated. The residue was analyzed by v.p.c. as described above. When cyclohexane was used the solution was filtered free from suspended pyrogallol before evaporation and hydride reduction. The decomposition of the peresters was shown to be complete by absence of carbonyl absorption in the initial product mixture and absence of cis- or trans-9-decalylcarbinols in the reduced products. In 1,2-dimethoxyethane the weight of crude products corresponded to 70–80% yields of hydroperoxides.

The Stereochemistry of the Pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecanes and -dienes. Norbornene and Norbornadiene Dimers

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Contribution from the Union Carbide Research Institute, Tarrytown, New York. Received January 12, 1965

Six of the possible twelve stereoisomeric pentacyclo-[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecanes and -dienes have been prepared, separated, and characterized. The structural assignments were made largely on the basis of a detailed study of the n.m.r. spectra.

The importance of the stereochemistry of a reaction product as a probe into the mechanism for its formation has been adequately demonstrated in the past. This is particularly true for norbornene where the double bond has one side (*exo*) less hindered than the other (*endo*) by virtue of strong steric shielding by the *endo* hydrogens on the ethylene bridge. Thus, reagents prefer to approach norbornene from the *exo* side.[2] The purpose of this work was to determine the stereochemistry of the norbornene and norbornadiene dimers. With this knowledge in hand it is possible to reflect upon the mechanism of the reactions for their formation. It should be noted that the stereochemistry of some of these isomers has been erroneously assigned[3a,b] and several times quoted[3c,d] in the recent past.

There are six possible stereoisomeric structures for a dimer of norbornene or norbornadiene, corresponding to three ways of specifying two possible configurations (*exo* or *endo*) in each of two norbornane fragments[4] and

two independent choices of juncture (*cis* or *trans*) to the four-membered ring; these are shown in rough projection formulas in Table I. All of the structures have a plane of symmetry; in addition 1, 2, 4, 5, 7, 8, 10, and 11 have a twofold axis. The point groups are as indicated in the table.

On the basis of molecular models and calculations reported below, structures 7, 10, and 11 are expected to be highly strained in order to relieve nonbonded repulsions between protons at 13, 14, or 5, 6, and 11, 12. The situation is more favorable in 12 since the opposing groups do not lie in the same plane, and possibly in 8 and 9 where the interactions involve π-electrons.

Pertinent to the possible existence of 8 is the isolation of a saturated norbornadiene dimer for which structure 13 is proposed.[3b,6] This structure could have 8 as a precursor.
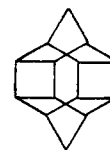
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Preparation of Dimers. The arguments that follow demonstrate that the stereochemistry of the dimers which have been prepared to date is that of structures 1 through 6 (Table I). The reactions used for the preparation of these dimers are summarized in eq. 1–7.[7] In addition, treatment of norbornadiene with phenyllithium is reported[8] to give a dimer (m.p. 33°) which

(1) Research and Development Department, Chemicals Division, Union Carbide Corp., South Charleston 3, W. Va.

(2) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *J. Am. Chem. Soc.*, 84, 2611 (1962), and references therein.

(3) (a) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind.* (London), 20 (1960); (b) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, 373 (1961); (c) D. Scharf and F. Korte, *ibid.*, 821 (1963); (d) G. N. Schrauzer and S. Eichler, *Ber.*, 95, 2764 (1962).

(4) Structures in which the cyclobutane ring is fused *trans* on the norbornane would be highly strained. There are several examples of a six-membered ring fused to a four-membered ring by a *trans* juncture but only a few examples of a five-membered ring fused to a four-membered ring by a *trans* juncture, and then only when the five-membered ring is flexible.[5]

(5) J. Meinwald, J. J. Tufariello, and J. J. Hurst, *J. Org. Chem.*, 29, 2914 (1964).

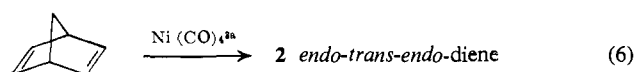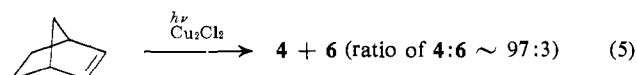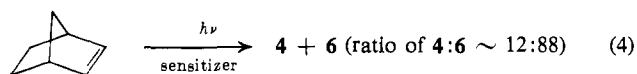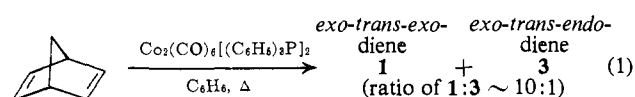(6) D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 368 (1961).

(7) We wish to thank Professor R. C. Cookson for providing samples of dimers 2 and 5.

(8) G. Wittig and J. Otten, *Tetrahedron Letters*, 601 (1963).

Table I. Stereochemistry of
Pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecanes and -dienes

1	**2**	**3**
exo-trans-exo-diene	endo-trans-endo-diene	exo-trans-endo-diene
m.p. 67–68°	m.p. 92–93°	m.p. (oil)
C$_{2h}$	C$_{2h}$	C$_s$

4	**5**	**6**
exo-trans-exo	endo-trans-endo	endo-trans-exo
m.p. 63.5–64°	m.p. 99–102°	m.p. 38–39°
C$_{2h}$	C$_{2h}$	C$_s$

7	**8**	**9**
exo-cis-exo-diene	endo-cis-endo-diene	endo-cis-exo-diene
C$_{2v}$	C$_{2v}$	C$_s$

10	**11**	**12**
exo-cis-exo	endo-cis-endo-	endo-cis-exo-
C$_{2v}$	C$_{2v}$	C$_s$

may be one of the remaining isomers; however, we have been unable to duplicate this preparation.

$$
\begin{array}{c}
\text{exo-trans-exo-} \quad \text{exo-trans-endo-}\\
\text{diene} \quad\quad \text{diene}
\end{array}
$$

$$\xrightarrow[\text{C}_6\text{H}_6, \ \Delta]{\text{Co}_2(\text{CO})_6[(\text{C}_6\text{H}_5)_3\text{P}]_2} \quad \mathbf{1} + \mathbf{3} \quad (1)$$

(ratio of 1:3 ∼ 10:1)

$$\mathbf{1} \xrightarrow[\text{Pd–C}]{\text{H}_2} \mathbf{4} \ \textit{exo-trans-exo} \quad (2)$$

$$\mathbf{3} \xrightarrow[\text{Pd–C}]{\text{H}_2} \mathbf{6} \ \textit{exo-trans-endo} \quad (3)$$

$$\xrightarrow[\text{sensitizer}]{h\nu} \mathbf{4} + \mathbf{6} \ (\text{ratio of } \mathbf{4}{:}\mathbf{6} \sim 12{:}88) \quad (4)$$

$$\xrightarrow{\overset{h\nu}{\text{Cu}_2\text{Cl}_2}} \mathbf{4} + \mathbf{6} \ (\text{ratio of } \mathbf{4}{:}\mathbf{6} \sim 97{:}3) \quad (5)$$

$$\xrightarrow{\text{Ni (CO)}_4{}^{3a}} \mathbf{2} \ \textit{endo-trans-endo}\text{-diene} \quad (6)$$

$$\mathbf{2} \xrightarrow{\text{H}_2} \mathbf{5} \ \textit{endo-trans-endo} \quad (7)$$

The dimerization of norbornadiene catalyzed by organometallic complexes is reported to give rise to the isomers **1** and **2** in varying ratios and yields depending upon the catalyst and the conditions of the reaction.[3a,b,d,9,10] For our purposes norbornadiene and hexacarbonylbis(triphenylphosphine)dicobalt(0) in benzene were refluxed for several hours (reaction 1) to afford the diene dimers **1** and **3** in the ratio of about 10:1. The exo-trans-endo-diene dimer **3** has not been reported previously. The pure dimers were obtained by preparative scale vapor phase chromatography.

The saturated dimers **4** and **6** were obtained by catalytic reduction (reactions 2 and 3) of the dienes **1** and **3**, thus establishing the correspondence between the two systems. The saturated dimers **4** and **6** were also prepared by the photosensitized dimerization of norbornene (reaction 4).[3c,11] This reaction involves, in an initial step, triplet–triplet transfer from a sensitizer to norbornene. The ratio of isomers **4** to **6** is about 12:88 and appears to be independent of the sensitizer (acetophenone, benzene, acetone, dicyclopropyl ketone, and cyclopropyl phenyl ketone) used.[12]

The dimerization of norbornene through the irradiation of the cuprous chloride complex (reaction 5) is the first example of an intermolecular ring closure by this method. Formally analogous cuprous chloride catalyzed photoreactions have been reported by Srinivasan.[13] He found that under these conditions butadiene and 1,5-cyclooctadiene closed intramolecularly to give cyclobutene and tricyclo[3.3.0.0^{2,6}]octane, respectively.[13] That this reaction does not involve a simple triplet–triplet transfer, such as reaction 4, is apparent from the high stereoselectivity of product formation, with **4** predominating to the extent of about 97%. The results of a study of the scope and mechanism of this interesting reaction will be reported elsewhere.[14]

To assist further in the determination of the stereochemistry of these isomers the 5,6,11,12-tetradeuterio derivatives of **4** and **6** were prepared by reactions 4 and 5 starting with 5,6-exo-exo-dideuterionorbornene. The catalytic reduction of norbornadiene with deuterium using palladium on carbon as catalyst afforded 5,6-exo-exo-dideuterionorbornene (reaction 8). A 63% yield

$$
\mathbf{13} \qquad\qquad\qquad\qquad (8)
$$
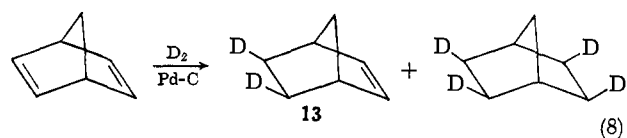
of the olefin **13** contaminated with the tetradeuterionorbornane and minor amounts of the starting diene, was realized by stopping the reduction after the uptake of 1.1 mole equiv. of deuterium. The dideuterionorbornene and tetradeuterionorbornane both have the deuterium primarily in the exo position as shown by n.m.r.[15] These would be the expected products if the less hindered

(9) R. Pettit, J. Am. Chem. Soc., 81, 1266 (1959).
(10) F. G. A. Stone, unpublished results.
(11) D. R. Arnold, R. L. Hinman, and A. H. Glick, Tetrahedron Letters, 1425 (1964).
(12) This reaction appears to be fairly general for small cyclic olefins. We have dimerized several norbornene derivatives and cyclohexene by this method. We have not been able to obtain dimers from noncyclic olefins: D. R. Arnold, unpublished results.
(13) R. Srinivasan, J. Am. Chem. Soc., 85, 3048 (1963); 86, 3318 (1964).
(14) D. J. Trecker, unpublished results.
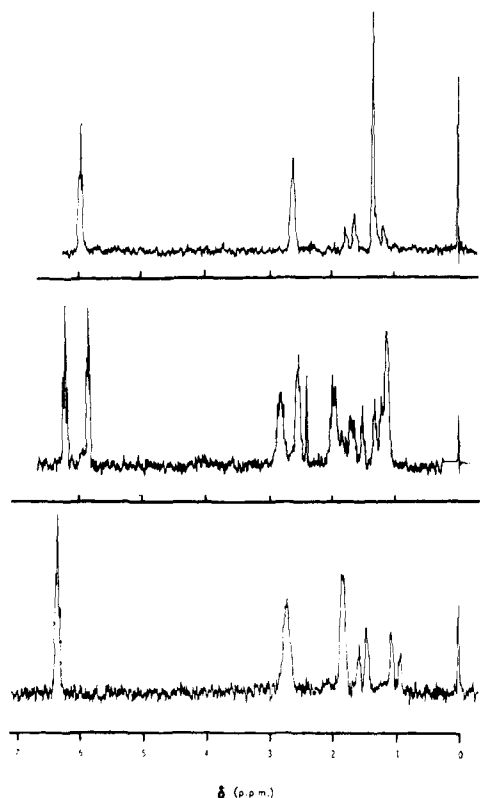(15) E. B. Whipple and D. R. Arnold, unpublished results.

Figure 1. H^1 magnetic resonance spectra (60 Mc.) of norbornadiene dimers: top, *exo-trans-exo;* center, *exo-trans-endo;* bottom, *endo-trans-endo.*

exo side of norbornene approaches the catalyst in preference to the *endo* side.[16]

Mass Spectra. The mass spectra[17] of **4**, **5**, **6**, tetradeuterio **4**, and tetradeuterio **6** were studied. All of these dimers showed prominent parent peaks as expected for their elemental composition. A major peak in the spectra of all of these dimers (even those with four deuterium atoms) appeared at m/e 91, characteristic of the $C_7H_7^+$ fragment. This is not a major fragment in the mass spectrum of norbornene.[18] One possible explanation for this unexpected result is loss of a C_2 fragment followed by rapid loss of a C_5 fragment (or *vice versa*) as shown in reaction 9. An examination of the metastable peaks lends support to this pathway.
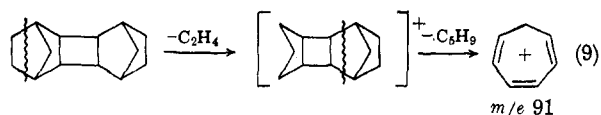
N.m.r. The proton magnetic resonance spectra of the diene dimers **1** through **3**, shown in Figure 1, limit the symmetry of **3** to C_s or lower, consistent only with an unsymmetrical pairing of norbornene fragments. Isomers **1** and **2** have simpler spectra, characteristic of a symmetrical coupling of fragments with typical n.m.r. parameters.[19] The spectrum of **1** is in accord with two

exocyclic junctures with the four-membered ring, while the spectrum of **2** indicates two endocyclic junctures. Thus, the configuration assigned previously[3,20] is shown to be inverted. In particular, **1** shows narrower lines than **2** both for the protons on the cyclobutane ring and on the bridgeheads, implying a weaker coupling between these nuclei. This is diagnostic of an endocyclic configuration of the *protons* at the juncture.[19,21] The order of the chemical shifts ($\delta_{endo} < \delta_{exo}$) of the juncture protons is also indicative of an endocyclic environment for protons in **2**. We accordingly assign as *exo-exo* configuration to **1** and an *endo-endo* configuration to **2**. Both are tentatively assumed to be *trans*.

As previously mentioned, catalytic hydrogenation of the diene dimers established that **4** has the same configuration as **1**, **5** the same as **2**, and **6** the same as **3**. The n.m.r. spectra of the saturated dimers, Figure 2, are consistent with this assignment. The spectrum of **6** suggests an unsymmetrical juncture by virtue of the fact that the integrated intensities of the three nearly resolved regions of the spectrum are in the approximate ratios 2:9:9. None of the four structures possessing a twofold axis of symmetry is compatible with an odd grouping of proton chemical shifts, since none of the protons lies on the symmetry axis.

It remained to establish whether **3** and **6** have a *cis* or *trans* juncture at the cyclobutane ring and to confirm the *trans* structures of **1**, **2**, **4**, and **5**. Since all have symmetry of the same order, further differentiation on the basis of n.m.r. spectra requires interpretation of the parameters involved. The coupling constants in the cyclobutane ring[22] would be very difficult to measure, while the chemical shifts in the unsaturated dimers are difficult to interpret in terms of simple models. For these reasons, the 5,6,11,12-tetradeuterio derivative of **6** was prepared and its n.m.r. spectrum, Figure 3, was investigated to permit a more detailed interpretation of the spectra in Figure 2.

The H^1 spectrum of the tetradeuterio dimer is completely resolved into two regions with an odd intensity distribution of 11:5. In addition to substantiating the unsymmetrical pairing of fragments, this means that at least one of the four methylene bridge protons is shifted to the low-field region of the spectrum. Also, four of the original nine high-field protons in the spectrum of **6** are identified by substitution as exocyclic hydrogens of the ethylene bridges. These protons should couple strongly, and hence the deuterons couple observably ($J_{HH}/J_{HD} \cong 6.5$), to geminal *endo* protons and to vicinal bridgehead hydrogens. Application of a decoupling field at the deuterium frequency (Figure 3b) narrows lines centered at 0.96 and 1.82 p.p.m. which are evidently due to the endocyclic ethylene bridge hydrogens and perturbs slightly the bridgehead proton bands at 2.20 and 1.95 p.p.m. The broader 2.20-p.p.m. band can be assigned to the bridgehead protons adjacent to exocyclic protons on the cyclobutane ring; hence on the fragment with the endocyclic juncture.

The two pairs of endocyclic ethylene bridge protons both give sharp doublets on decoupling the geminal deuterons in Figure 3. Moreover, proton–proton decoupling experiments both with and without simul-

(16) Similar results were observed upon catalytic reduction of norcamphor: S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956).

(17) G. G. Meisels and D. R. Arnold, to be published.

(18) American Petroleum Institute Research Project 44, "Catalog of Mass Spectra Data," Agricultural and Mechanical College, Texas, College Station, Texas, 1960, No. 1774.

(19) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

(20) See also M. Green and E. A. C. Lucken, *Helv. Chim. Acta*, **45**, 1870 (1962).

(21) F. A. L. Anet., *Can. J. Chem.*, **39**, 789 (1961).

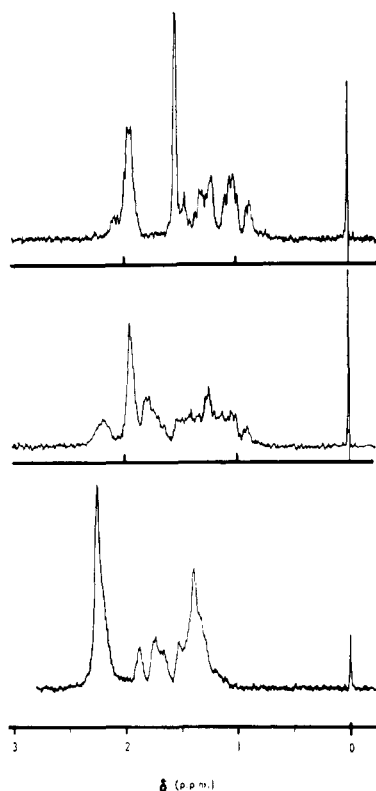(22) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

Figure 2. H^1 magnetic resonance spectra (60 Mc.) of norbornene dimers: top, *exo-trans-exo;* center, *exo-trans-endo;* bottom, *endo-trans-endo.*
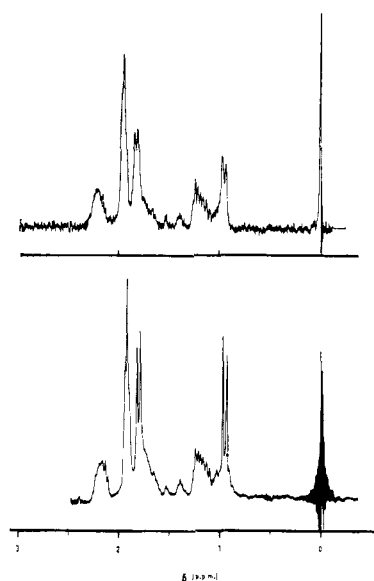

Figure 3. H^1 magnetic resonance spectrum (60 Mc.) of photo-dimer of norbornene-5,6-d_2. H^1 spectrum (bottom) with H^2 decoupled.

taneous deuteron irradiation show that the nucleus responsible for the splitting of each has very nearly the frequency of the other. It is very unlikely that the two groups of endocyclic ethylene bridge hydrogens are mutually coupled, since one would then expect some visible manifestation of virtual coupling. What instead appears to be the case is that single methylene bridge protons are separately responsible for the splittings and that the shift of each accidentally happens to coincide nearly with that of the pair of endocyclic protons coupled to the other. The integrated intensities in Figure 3 are consistent with this interpretation, requiring that at least one bridge proton be in each resolved region of the spectrum. By analogy to other norbornane and norbornene systems, the configurations of the methylene bridge protons responsible for the splittings would be *anti* to the ethylene bridges, or *syn* to the four-membered ring.[23]

If correct, these arguments would imply that the methylene bridge proton *anti* to the cyclobutane ring and in the norbornane fragment with the endocyclic ring juncture would be coupled only to a geminal bridge proton responsible for one of the doublets in Figure 3, and to the pair of bridgehead protons at 2.2 p.p.m. A double-resonance experiment in which the indicated bridgehead band is continuously irradiated while the observing frequency is swept through the spectrum (Figure 4) identifies the methylene proton as the pair of lines or pair of triplets in Figure 3, with a chemical shift of 1.3 p.p.m. The order of component intensities shows the coupled ($|J| \cong 9.3$ c.p.s.) geminal proton to be at higher field by 0.1 p.p.m. and hence responsible
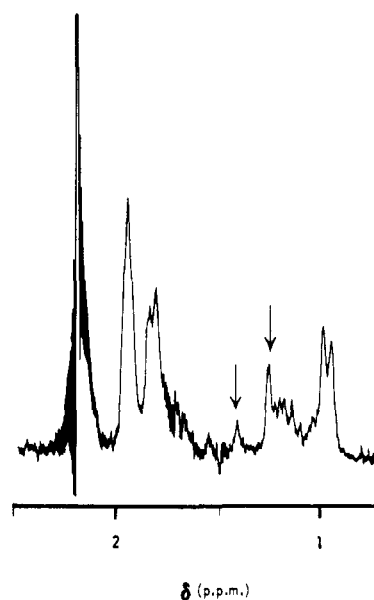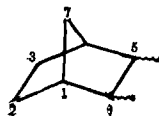

Figure 4. H^1 spectrum (frequency sweep) of norbornene-5,6-d_2 photodimer with low-field band irradiated.

for the splitting of the low-field pair of endocyclic ethylene bridge protons. One can thus assign chemical shifts individually to all the protons except those on the four-membered ring of the d_4-dimer. The mean chemical shift can be determined[24] from the centroid of the spectrum, so that by subtracting out the known values one arrives at an average shift of 1.8 p.p.m. for the two cyclobutane ring proton shifts in the d_4-dimer. Similarly, the average shift of the two pairs of exocyclic ethylene bridge protons can be measured from the difference in centroids between the normal and partially deuterated dimers. The chemical shifts in the symmetrical dimers were more or less evident from inspection of the spectra, once those of the unsymmetrical

(23) J. I. Musher, *Mol. Phys.,* **6,** 93 (1963).

(24) E. B. Whipple and M. Ruta, *J. Am. Chem. Soc.,* in press.

Table II. Chemical Shifts in Norbornene Derivatives[a]

Compd. no.	Compd.		δ_1	δ_2	δ_6	δ_7 syn	δ_7 anti
	Norbornene		2.83	5.96	1.53 (exo) 0.95 (endo)	1.06	1.32
	Norbornadiene dimer						
1	(exo-trans-exo)		2.62	5.97	1.32	1.69	1.23
3	(exo-trans-endo)	exo fragment	2.54	5.82	1.13		
		endo fragment	2.80	6.20	2.0		
2	(endo-trans-endo)		2.72	6.35	1.85	1.02	1.55
				1.41 (exo)		1.18	1.18
	Norbornane		2.22	1.18 (endo)			
	Norbornene dimer						
4	(exo-trans-exo)		1.93	0.95	1.54	1.95	1.13
6	(exo-trans-endo)	exo fragment	1.95	1.5 (exo)[b] 0.96 (endo)	1.8[b]	1.8	1.2
		endo fragment	2.20	1.5 (exo)[b] 1.82 (endo)		1.0	1.3
5	(endo-trans-endo)		2.25	1.25–1.5 (exo) 1.8 (endo)	2.25	1.25–1.5	1.25–1.5
	Norbornadiene		3.55	6.7		2.0	2.0

[a] In p.p.m. [b] Mean value for both fragments.

dimer were known. The chemical shifts are summarized in Table II.

The first conclusion apparent from the data in Table II is that, apart from the protons on the four-membered ring juncture, the chemical shifts of the protons on each norbornane fragment are largely independent of the configuration of the other. The second conclusion is that the shifts relative to norbornane are small in all positions except where close approach to the opposite fragment occurs, i.e., except for endocyclic protons on endo-substituted fragments and for methylene bridge protons syn to exocyclic substitution. There are several recognized ways in which a close-neighboring, non-bonded group can affect directly the shielding of a proton. These include anisotropy in the magnetic susceptibilities of bonds,[25] polarization due to the reaction field about neighboring charge centers,[26] and intramolecular van der Waals interactions.[27] While the absence of detailed structural information only permits illustrative calculations of specific contributions to be made, these tend to confirm the apparent fact that cis structures are incompatible with the observed independence of shift on configuration of the opposite fragment. The norbornane skeletons are much further apart in the trans structures, however, so that the observed proton shifts can be explained by more or less constant interactions with the bonds directly involved in or attached to the cyclobutane ring.

Structures were estimated by assuming two norbornane fragments with structures computed by Wilcox[28] to be trans coupled by a planar, four-membered ring with standard C–C (1.54 Å.) and C–H (1.10 Å.) bond lengths, and with three equal H–C–C

bond angles at each corner of the ring juncture. The remaining unspecified C–C–C angles between the norbornane skeletons and the cyclobutane rings were assigned the reasonable value of 118°. Using as a model point dipoles located at the centers of the respective bonds, the contributions[25] from C–C and C–H magnetic anisotropy were calculated using values obtained by Zurcher[29] for $\chi_{||} - \chi_{\perp}$, and the reaction field contribution was[26] calculated for C–H dipoles of 0.4 D. The calculated contributions ($\sim$0.4 p.p.m.) from carbon–carbon and carbon–hydrogen bond anisotropies[29] are in the opposite direction from the shifts observed. This together with the rather small (<2 Å.) interproton distances depicted in 14 and 15 below suggest that intramolecular van der Waals forces are the principal factor responsible for the low-field shifts, and crude models[27] do predict contributions of the order of parts per million from this source. The calculated contributions δ_1 and δ_2 below compare better when allowance is made for puckering of the cyclo-butane rings.

One would expect intramolecular van der Waals shifts to be reciprocated in the cyclobutane ring protons, and there is evidence that this is so. As was pointed out before, the average cyclobutane proton shift in the unsymmetrical dimer is equal within error to the mean of the corresponding shifts in the two symmetrical dimers. Two variable contributions to the shifts of these protons are expected, one due to their immediate exocyclic or endocyclic environment, and one due to nonbonded
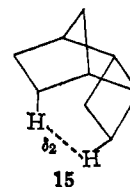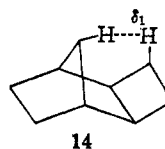
(25) J. A. Pople, Proc. Roy. Soc. (London), A239, 541, 550 (1957); H. M. McConnell, J. Chem. Phys., 27, 226 (1957).
(26) A. D. Buckingham, Can. J. Chem., 38, 300 (1960).
(27) T. Schaefer, W. F. Reynolds, and Y. Yonemoto, ibid., 41, 2969 (1963).
(28) C. F. Wilcox, Jr., J. Am. Chem. Soc., 82, 414 (1960).

14

15

(29) P. F. Zurcher, J. Chem. Phys., 37, 2421 (1962).

interaction with the nearest proton on the other nor-bornane skeleton (δ_1 or δ_2 in **14** or **15**). From the two symmetrical dimers, one obtains

$$(\delta_{exo} - \delta_{endo}) + (\delta_2 - \delta_1) =$$
$$2.25 - 1.54 = 0.71 \text{ p.p.m.}$$

Since $\delta_{exo} - \delta_{endo}$ in norbornane is 0.25 p.p.m., the indicated value of $\delta_2 - \delta_1$ is 0.45 p.p.m. Were the interactions in **14** and **15** truly reciprocal a difference of 0.3 p.p.m. would have been expected from the observed values, $\delta_2 = 2\delta_1 = 0.6$ p.p.m. While reciprocity need not be exact, its very presence is another strong argument against any *cis* structure.

It is of interest to reconsider the spectra of the unsaturated dimers in view of these results. The chemical shifts generally are more dependent on the configuration of the other fragment than was the case with the saturated dimers. This is probably due to anisotropic contributions from the more polarizable double bonds. However, the main trends observed in the saturated dimers are repeated, *e.g.*, the bridgehead protons are shifted only by exocyclic substitution, and the methylene bridge proton *syn* to an exocyclic juncture undergoes a strong paramagnetic shift (0.6 p.p.m.). The vinyl protons are shifted to lower field by an endocyclic juncture, but much less so than are the endocyclic ethylene bridge protons of the saturated dimers. This would be expected, since the internuclear distances are greater in the unsaturated compounds. The cyclobutane ring protons opposite an exocyclic fragment are presumably shifted to lower field by the same interaction with a methylene bridge proton as before (0.3 p.p.m.), but when opposite an *endo* fragment no longer undergo the strong paramagnetic shift due to close approach of an *endo* proton. The double bond may, of course, introduce some new contribution. Taking the difference in cyclobutane proton shifts opposite *exo* and *endo* fragments (0.18 p.p.m.) as the difference in contributions from a *syn* methylene bridge proton (0.3 p.p.m.) and the vinyl group, a paramagnetic shift of 0.12 p.p.m. is attributed to the latter. Similar comparisons show that the differences between *exo* and *endo* shifts are larger than in saturated dimers, as expected.[30]

Experimental

Reaction of Norbornadiene with Hexacarbonylbis-(triphenylphosphine)dicobalt(0). Norbornadiene (270 g., 2.93 moles, b.p. 89–90°), benzene (240 g., dried and redistilled), and hexacarbonylbis(triphenylphosphine)-dicobalt(0)[31] (6 g., 0.0074 mole) were stirred together under reflux for 48 hr. The reaction mixture was then washed with dilute hydrochloric acid and separated, and the aqueous portion was twice extracted with ether. The combined · organic portions were washed with aqueous sodium carbonate, dried over anhydrous sodium carbonate, filtered, and evaporated. Analysis of the residual liquid by gas chromatography[32] showed that the volatile portion consisted of 84% **1**, 8% **3**, and 8% of other products.[33] Careful fractionation on a 24-in. spinning-band column afforded a total of 26.5 g.

(0.144 mole, 10% yield) of dimers (center cut, b.p. 115–117° at 10 mm.). Further separation was carried out by preparative-scale gas chromatography.[34]

Dimer **1**, shown to be >99% pure by v.p.c.[32] analysis, melted at 67–68°. Its infrared spectrum had maxima characteristic of the norbornene double bond (ν_{max} 1562 and 707 cm.$^{-1}$).[35] It took up 1.97 moles of hydrogen per mole of product (theory, 2.00).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.57; H, 8.40.

Dimer **3** was a clear oil which analyzed for 96% purity by v.p.c.[32] Its infrared spectrum also had the expected norbornene double bond absorptions (ν_{max} 1560 and 707 cm.$^{-1}$).[35] It took up 1.96 moles of hydrogen per mole of product (theory, 2.00).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.13; H, 8.67.

Hydrogenation of **1** *and* **3**. A small sample of **1** (0.59 g.) was taken up in ethanol (100 ml.) and hydrogenated over palladium on charcoal in the usual fashion. The catalyst was filtered off, and the reaction mixture was evaporated under reduced pressure to afford white needles (0.56 g.). After a recrystallization from ethanol, the needles (dimer **4**) melted at 63.5–64°. The infrared and n.m.r. spectra, which were compatible with the structure of compound **4**, were used for comparison with the corresponding spectra of the photodimer. V.p.c. analysis[32] showed **4** to be >98% pure.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.31; H, 10.91.

A sample of **3** was similarly reduced. Work-up afforded white plates which, after recrystallization from ethanol, melted at 38–39°. The infrared and n.m.r. spectra of **6** were used for comparison with corresponding spectra of the photodimer. Compound **6** was shown to be 96% pure by v.p.c. analysis.[32]

Cuprous Chloride Catalyzed Photodimerization of Norbornene. Norbornene (493 g., 5.24 moles), ether (100 ml., anhydrous), and cuprous chloride (2.0 g., 0.014 mole) were stirred together under nitrogen until solution was complete. The solution was then filtered and added to a tubular reactor which was fitted with a concentric, water-jacketed Vycor immersion finger containing a 450-w. Hanovia medium-pressure mercury arc. The reactor was equipped with a brine-cooled reflux condenser, a thermocouple well, a septum-capped outlet for sample withdrawal, and a fritted-glass disk at the bottom of the reactor for nitrogen ebullition. The solution was irradiated with continuous nitrogen purge for 145 hr. Temperature was maintained at 29 ± 2°. After the irradiation was completed, the reaction mixture was filtered and evaporated under reduced pressure to a viscous residue (87 g.). Sublimation under reduced pressure afforded white crystals (65.4 g., 0.348 mole, 14.5% yield), which were shown by v.p.c. analysis[32] to consist of >97% of **4**. The crystals were taken up in ethanol and evaporated to a mass of fine, white needles. The needles melted at 64–64.5°. The mixture melting point with the hydrogenation product of **1** was undepressed (64–64.5°).

(30) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).
(31) W. Hieber and J. Sedlmeier, *Chem. Ber.*, **87**, 789 (1954).
(32) Poly[diethanolaminesuccinate] on Chromosorb W column (10 ft.), 160°, helium gas.
(33) These were apparently the other dimers and trimer described in Belgian Patent 626,407 (Dec. 21, 1962), to Shell.

(34) Wilkens A-700 Autoprep, poly[diethanolaminesuccinate] on Chromosorb W column (20 ft.), 195°, helium gas.
(35) R. C. Lord and R. W. Walker, *J. Am. Chem. Soc.*, **76**, 2518 (1954); P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71; mol. wt., 188. Found: C, 89.37; H, 10.71; mol. wt., 190.

The infrared and n.m.r. spectra of the photodimer **4** were identical with the corresponding spectra of the hydrogenation product of **1** to the smallest detail.

Photosensitized Dimerization of Norbornene. A solution of norbornene (320 g., 3.41 moles), acetophenone (41 g., 0.34 mole), and benzene (150 ml.) was charged to the reactor previously described. A Pyrex immersion finger replaced the Vycor finger containing the mercury arc. Irradiation was carried out for 192 hr. with continuous nitrogen ebullition. The reaction temperature was maintained at 29 ± 2°. After the irradiation was completed, the benzene, acetophenone, and unreacted norbornene were removed by distillation. The residual liquid, analyzed by v.p.c.,[32] contained dimers **4** and **6** in a 12:88 ratio, in addition to small amounts of higher boiling products. Careful fractionation on an 18-in. spinning-band column afforded 11 cuts of dimer (boiling range 92–110° at 3 mm., 72.2 g., 0.768 mole, 23% yield). The fraction boiling at 100–102° at 1 mm. was shown to be pure **6** by v.p.c. analysis.[32] This fraction crystallized upon standing to give clear plates that melted at 38.5–39.5°.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71; mol. wt., 188. Found: C, 89.57; H, 10.51; mol. wt., 191.

The mixture melting point of **6** with the hydrogenation product of **3** was undepressed (38–39°). The infrared and n.m.r. spectra of the two were identical.

Catalytic Reduction of Norbornadiene. A solution of norbornadiene (2.30 g., 0.025 mole) in benzene (50 ml.) to which palladium on carbon (5%, 0.1 g.) had been added was stirred under a deuterium atmosphere. The reaction was stopped when the uptake of deuterium was equiv-

alent to 1.1 moles. The solution was filtered from the catalyst and brought back to the original volume by the addition of benzene. Analysis by v.p.c. showed only a trace of norbornadiene remaining with dideuterionorbornene equivalent to a 63% yield, the rest being tetradeuterionorbornane. This solution was used in the acetophenone-sensitized dimerization without further purification. In the case of the cuprous chloride catalyzed dimerization ether replaced benzene as the solvent for reduction. Pure samples of dideuterionorbornene and tetradeuterionorbornane for n.m.r. were obtained by preparative-scale gas chromotography.[36]

N.m.r. Spectra. N.m.r. spectra were measured on a Varian A-60 spectrometer operating in a V-4012-SM 12-in. magnet gap. The heteronuclear double resonance experiments were conducted using an HR-60 spectrometer and an NMR Specialties HD-60 spin decoupler. Homonuclear field-sweep decoupling experiments were carried out by addition of a 1200-c.p.s. audio side-band detector similar to that described by Johnson.[37] A somewhat similar unit with an added 2-kc. tuning fork oscillator served as a field-frequency locking system in the manner described by Primas,[38] and Freeman and Anderson.[39] For frequency-swept experiments the 1200-c.p.s. oscillator driving the first side-band detector was replaced with a General Radio Type 1107-A interpolation oscillator modified for motor drive.

(36) Wilkens A-700 Autoprep silicon oil SE-30 (30%) on Chromosorb P column (20 ft.), 100°, helium gas.

(37) L. F. Johnson in "NMR and EPR Spectroscopy," Varian Associates Staff and Consultants, Pergamon Press, Inc., New York, N. Y., 1960, p. 187.

(38) H. Primas, Fifth European Congress on Molecular Spectroscopy, Amsterdam, 1961.

(39) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

Oxidative Cleavage of Cyclopropanes. III.[1,2] The Stereochemistry and Direction of Cleavage of Bicyclo[n.1.0]alkanes by Lead Tetraacetate and Thallium Triacetate

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The direction and stereochemistry of the oxidative cleavage of the cyclopropane bond by lead tetraacetate and thallium triacetate has been determined by utilizing bicyclo[4.1.0]heptane, bicyclo[3.1.0]hexane, and bicyclo[2.1.0]pentane. The facility of bond cleavage increases as the strain of the system increases. Products resulting from internal bond cleavage increase with decreasing ring size. External bond cleavage yields exclusively trans-2-acetoxymethylcycloalkyl acetates. Internal bond cleavage results in the formation of unsaturated monoacetates and 1,3-diacetates. The stereochemistry of the diacetates that result from internal bond cleavage is a function of the mode of decomposition of the intermediate organometallic derivative. Oxidative cleavage of cyclopropanes is postulated to occur via a two-step process in which electrophilic attack of the metal salt results in the formation of an organometallic derivative, which then solvolytically decomposes. The apparent rate of electrophilic attack of lead tetraacetate is slower than that of thallium triacetate, while the rate of decomposition of the organolead intermediate is faster than that of the organothallium intermediate.

(1) Part I: R. J. Ouellette and D. L. Shaw, *J. Am. Chem. Soc.*, **86**, 1651 (1964); part II: R. J. Ouellette, D. L. Shaw, and A. South, Jr., *ibid.*, **86**, 2744 (1964).

(2) Initial research was carried out with partial support of a Petroleum Research Fund Starter Grant. This research was also supported by Grant-GP 3873 from The National Science Foundation.