

TABLE VI
RATE CONSTANTS FOR THE DEHYDROBROMINATION OF THE 2,3-DIBROMONORBORANES WITH SODIUM *t*-AMYLOXIDE IN *t*-AMYLOL ALCOHOL

Init. concn., moles/l. $\times 10^2$	Init. concn. of base, mole/l.	$T, ^\circ\text{C}.$ $\pm 0.05^\circ$	$k \times 10^4$, l./mole/sec.	Av. $k \times 10^4$
<i>endo-cis</i> -2,3-Dibromonorbornane (I)				
3.412	0.4903	96.5	6.35	
2.562	.4903	96.5	6.28	6.15 \pm 0.2
2.587	.4894	96.5	5.82	
3.472	.3293	106.8	13.17	
2.524	.3263	106.8	13.27	13.12 \pm 0.1
2.669	.3263	106.8	12.91	
<i>trans</i> -2,3-Dibromonorbornane (V)				
4.07	0.3068	56.07	14.42	
3.64	.3068	56.07	14.95	14.47 \pm 0.3
2.96	.2954	56.07	14.04	
3.340	.2918	45.89	5.06	
3.187	.2918	45.89	5.43	5.17 \pm 0.2
3.661	.2774	45.89	5.02	

The analysis for deuterium content³² of starting material and recovered material are given in Table III.

Assuming that the proton containing species is monodeuterated, the following expressions are derived

$$(-d[D]/dt) = k_D[D][B]; \quad (-d[H]/dt) = 1/2k_{11}[H][B] + 1/2k_H[H][B]$$

where [H] = concn. of monodeuterated species and [D] = concn. of dideuterated species. Dividing and integrating, one can obtain

$$\log(H_0/H) = [(k_H + k_D)/2k_D] \log(D_0/D) \quad (1)$$

From eq. 1 and the observed deuterium analysis it is possible to show that the amount of enrichment in deuterium content is con-

(32) Deuterium analyses are by J. Nemeth, Noyes Chemical Laboratory, Urbana, Ill., and are reported to be 1% relative with scattering to 2% relative.

sistent—within the limit of analysis—with the expected isotope effect, and corresponds to essentially no exchange.

Kinetic Isotope Effects.—From the kinetic data given in Table VII for the deuterated compounds, k_D (obsd.) was measured. Corrections for the amount of monodeuterated (assumed) contaminant can be made from eq. 2 and 3.

$$(d[\text{Br}]/dt) = k_D[D][B] + 1/2k_D[H][B] + 1/2k_H[H][B] \quad (2)$$

$$k_{\text{obsd.}} = k_D[D] + 1/2k_D[H] + 1/2k_H[H] = k_D[D] + 1/2[H](k_D + k_H) \quad (3)$$

TABLE VII
RATE CONSTANTS FOR THE DEHYDROBROMINATION OF THE DIDEUTERATED 2,3-DIBROMONORBORANES WITH SODIUM 1-PENTOXIDE IN 1-PENTANOL

Compd.	Concn., moles/l. $\times 10^2$	Concn. base, mole/l.	$T, ^\circ\text{C}.$ $\pm 0.03^\circ$	$k'_D \times 10^4$, l./mole./sec.	Av. k'
I-2,3- d_2 (1.91D)	2.630	0.1123	126.7	4.09	4.12 \pm 0.03
V-2,3- d_2 (1.90D)	1.820	.1123	126.7	4.14	
	3.322	.4688	96.3	7.43	7.45 \pm 0.02
	2.612	.4688	96.3	7.46	

An isotope effect at 123° was determined for *endo-cis*-2,3-dibromonorbornane (I) by allowing a sample of a known mixture of undeuterated I and monodeuterated I (prepared by the addition of DBr to 2-bromo-2-norbornene) to react to partial completion. Unreacted starting material was recovered as described above and was analyzed for deuterium content. The % reaction was determined by Volhard titration. The following data were recorded.

Atom, % D—	Concn. base, mole/l.	Concn. compd., moles/l. $\times 10^2$	Reacn., %	k_H/k_D	
Start	Recovd.				
4.20	4.77	0.4683	3.51	40.7	3.81 \pm 0.6
4.20	5.02	0.4683	3.51	51.6	4.04 \pm 0.6

The value for the isotope effect may be calculated from eq. 4.

$$\log(H_0/H) = [2k_H/k_H + k_D](\log D_0/D) \quad (4)$$

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, UNION CARBIDE CHEMICALS CO., SOUTH CHARLESTON 3, W. VA.]

Free-Radical Additions to Norbornadiene

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Addition of a number of addends with low chain-transfer constants to norbornadiene,¹ under free-radical conditions, leads to the corresponding nortricyclene² derivatives as the sole 1:1 adducts. Addition of thiophenol, a reagent with a high chain-transfer constant, gives rise to 5-norbornen-2-yl phenyl sulfide, the unrearranged adduct, as well as the nortricyclene derivative. The propensity of the 6-norbornen-2-yl radical (III) to rearrange to the 5-nortricyclyl radical (IV) is related to measured chain-transfer constants. Competitive addition of the trichloromethyl radical to a mixture of norbornadiene and norbornene demonstrates that the effect of the second double bond is strictly an additive one. No lowering of energy by means of a homoconjugative transition state (V) is indicated. Dipole moment studies of 3-dichloromethylene-5-chloronortricyclene indicate that the 5-chloro position is *exo* to the methylene bridge. This strongly suggests that chlorine abstraction by the 3-trichloromethyl-5-nortricyclyl radical is governed by steric considerations.

Introduction

Reactions involving homoconjugative addition of reactive intermediates to bicyclic olefins have received considerable attention in recent years.³⁻⁸ With interest focused primarily on the nature of the ionic intermediates, investigators have studied rearrangements

resulting from addition of numerous addends⁹ to norbornadiene. These rearrangements^{10,11} lead to 2,7-disubstituted-5-norbornenes and 3,5-disubstituted nortricyclenes and have been rationalized in terms of intermediates which may be conveniently represented by I and II.³

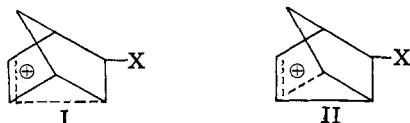
While ionic additions of this sort have been exhaustively investigated, analogous free-radical reactions

- (1) Bicyclo[2.2.1]hepta-2,5-diene.
- (2) Tricyclo[2.2.1.0^{2,5}]heptane.
- (3) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956); *Chem. Ind. (London)*, 56 (1956).
- (4) L. Schermerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956); H. Bluestone, S. B. Soloway, J. Hyman, and R. E. Lidov, U. S. Patents 2,730,548 (Jan. 10, 1956), 2,738,356 (March 13, 1956), 2,782-238 (Feb. 19, 1957).
- (5) G. T. Youngblood, C. D. Trivette, Jr., and P. Wilder, Jr., *J. Org. Chem.*, **23**, 684 (1958).
- (6) N. A. Milas and P. P. Otto, *ibid.*, **25**, 2225 (1960).
- (7) R. P. Arganbright and W. F. Yates, *ibid.*, **27**, 1205 (1962).
- (8) J. B. Miller, *ibid.*, **26**, 4905 (1961).

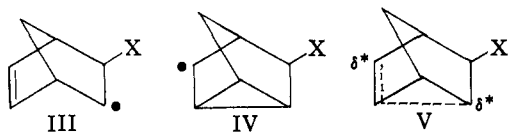
(9) Among the reagents which have been added to norbornadiene are bromine,^{3,4} chlorine,^{3,7} hydrogen bromide,^{3,7} hydrogen chloride,^{3,7} *p*-toluenesulfonyl chloride,³ mercuric acetate,³ *t*-butyl hydroperoxide (acid-catalyzed),⁸ water,⁵ methanol,⁵ performic acid (acid-catalyzed),⁵ and nitrosyl chloride.⁸

(10) Ionic rearrangements of this sort are reviewed by P. D. Bartlett in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 63-70.

(11) P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958), and references therein.



have received relatively little attention.¹² Cristol and co-workers¹⁵ have reported that *p*-thiocresol adds readily to norbornadiene to give a mixture of *exo*-5-norbornen-2-yl *p*-tolyl sulfide and 3-nortricyclyl *p*-tolyl sulfide. A recent patent disclosure¹⁷ described the light-induced addition of hydrogen sulfide to norbornadiene. With addends *p*-toluenesulfonyl chloride,¹⁸ perfluoropropyl iodide,¹⁹ and bromotrichloromethane,¹⁹ the corresponding 3,5-disubstituted nortricyclenes were obtained. Both Cristol and Reeder¹⁸ and Brace¹⁹ have suggested that, in these cases, the rearrangement of III to IV may be faster than the chain-transfer step leading to a stable 1:1 adduct. Here, a rearrangement



of one classical free radical to another is assumed, rather than a mesomeric intermediate of the type V.

The present investigation was undertaken to obtain a more systematic picture of the addition of free radicals to norbornadiene. Further qualitative and some quantitative evidence regarding the role of the chain-transfer step in the rearrangement of the 6-norbornen-2-yl radical was sought.

Results

The free-radical additions of carbon tetrachloride, chloroform, butanal, heptanal, diethyl phosphite, and thiophenol to norbornadiene have been carried out under a variety of conditions. The results are summarized in Table I.

The major product in all cases was the 1:1 adduct. Higher telomers in the form of viscous residues accounted for the remainder of the reaction product. With but one exception, the 1:1 adducts were shown to consist solely of the corresponding nortricyclene derivatives. Only with thiophenol was any norbornene derivative isolated. Structures for all adducts were assigned on the basis of elemental analyses, molecular weight determinations, and infrared and nuclear magnetic resonance spectroscopy. Infrared and n.m.r. spectral data are compiled in Tables IV and V.

In every instance the characteristic nortricyclene absorption band at 807 cm^{-1} ^{20,21} was present in the infrared. This has been attributed to a "cage-breathing" deformation by Lippincott²² and seems to apply, without exception, to all nortricyclene skeletons.^{21,23}

(12) Bicyclic olefins have been quite amenable to radical addition reactions. Szwarc¹⁴ has shown that norbornadiene has a "methyl affinity" between five and six times that of 1,4-cyclohexadiene. Moreover, norbornene was shown to be five times more susceptible to $\cdot\text{CCl}_3$ attack than cyclohexene.¹⁴ This reactivity may be attributed in part to "destabilization" energy imparted to double bonds by the added strain of a methylene bridge.¹⁵ This is reflected in heats of hydrogenation measurements of a series of monocyclic and bicyclic olefins.¹⁶

(13) A. Rajbenbach and M. Szwarc, *Proc. Chem. Soc.*, 347 (1958).

(14) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

(15) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

(16) R. B. Turner, W. R. Meador, and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

(17) J. E. Mahan and R. P. Louthan, U. S. Patent 3,019,267 (January 20, 1962).

(18) S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961).

(19) N. O. Brace, *ibid.*, **27**, 3027 (1962).

(20) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(21) G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962).

(22) E. R. Lippincott, *J. Am. Chem. Soc.*, **73**, 2001 (1951).

TABLE I

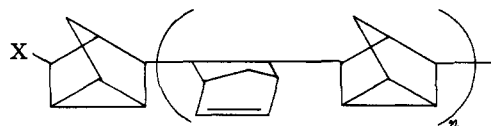
Addend (X-Y)	Addend-diene molar ratio	Initiator	Yield, %	
			of A	of B
$\text{CCl}_3\text{-Cl}$	4:1	Bz.P. ^a	67.3	None
$\text{CCl}_3\text{-H}$	4:1	Bz.P. ^a	60.0	None
$(\text{EtO})_2\text{P-H}$	4:1	T.B.P. ^c	51.4	None
$\text{C}_6\text{H}_5\text{C(=O)-H}$ (1)	4:3 ^b	T.B.P. ^c	52.0	None
$\text{C}_3\text{H}_7\text{C(=O)-H}$ (2) ^b	3:1	Bz.P. ^a	44.9	None
$\text{C}_3\text{H}_7\text{C(=O)-H}$ (3) ^b	4:1	Bz.P. ^a	44.2	None
$\text{C}_6\text{H}_5\text{S-H}$	4:1	Bz.P. ^a	46.3	None
$\text{C}_6\text{H}_5\text{S-H}$	1:1	None	71.5	19.0

^a Benzoyl peroxide. ^b Diene-peroxide solution added dropwise during course of reaction. ^c Di-*tert*-butyl peroxide.

Moreover, absorption doublets, appearing in each adduct at ~ 1457 and ~ 1300 cm^{-1} , are characteristic of 3-substituted nortricyclene derivatives.²¹ Nuclear magnetic resonance spectra were consistent with assigned structures in every instance. Chemical shifts assignable to various protons are discussed in the Experimental section.

It is significant that olefinic protons were detected in the n.m.r. spectrum of *only* the thiophenol-norbornadiene reaction product. The signals in the 4 τ region, characteristic of norbornene protons,⁸ were absent from the spectra of all other adducts. Further evidence against the formation of 5,6-disubstituted norbornenes was the absence of well-established norbornene C=C stretching and C-H deformation frequencies (1570 cm^{-1} region and 708 cm^{-1} region^{22,24}) in the infrared spectra of all adducts, except those from the thiophenol reaction. Moreover, gas chromatography columns, shown by independent experiments to be capable of resolving the two isomers,²⁵ gave only a single peak in the analysis of each adduct distillate. 5-Norbornen-2-yl phenyl sulfide, the only 5-substituted norbornene obtained, exhibited all of the spectral characteristics expected and was, moreover, resolvable from its nortricyclene isomer by v.p.c.

The higher telomers probably consist of the repeating units shown below. Zutty²⁶ has indicated the probability of alternating norbornenyl and nortricyclyl units in the free-radical homopolymerization of norbornadiene.



Infrared spectra of the telomeric residues, with bands at 807 (nortricyclene)²¹ and 707 cm^{-1} (norbornene),²⁴ are consistent with the suggested structure.

(23) 1-Substituted nortricyclenes, however, absorb in the region 840-850 cm^{-1} : H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959); H. Hart and R. A. Martin, *J. Am. Chem. Soc.*, **82**, 6362 (1960); L. Kaplan, H. Kwart, and P. R. Schleyer, *ibid.*, **82**, 2342 (1960).

(24) R. C. Lord and R. W. Walker, *ibid.*, **76**, 2518 (1954).

(25) An Aerograph Model A-110-C, employing a 10-ft. column of Carbowax 6000 on Chromosorb W, was used.

(26) N. L. Zutty, *J. Polymer Sci.*, **A1**, 2231 (1963).

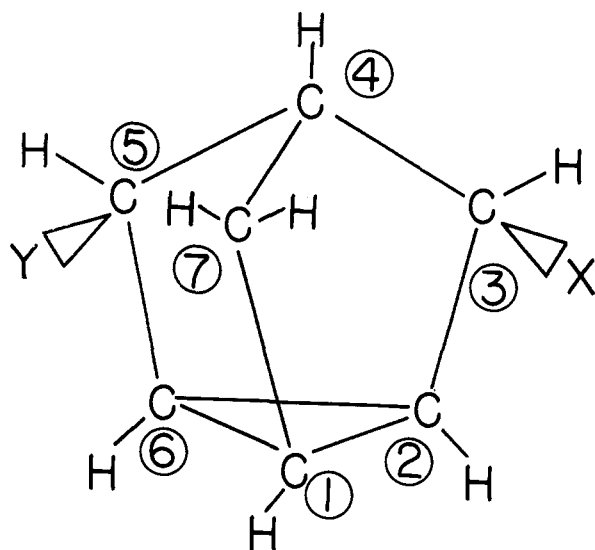


Fig. 1.—The Lippincott model²² of norbornadiene with carbons appropriately numbered.

Complications from competitive decarbonylation reactions resulted when aldehydes were used as addends. Butanal, when treated with norbornadiene and benzoyl peroxide at 78°, gave rise to 3-propylnorbornadiene (2.8%), as well as the expected addition product 3-butanoylnorbornadiene (42.7%). 4-Heptanol (1.4%) was also formed, presumably by means of a short chain reaction involving attack of a propyl radical on butanal.²⁷ Mechanisms which are involved in aldehyde decarbonylation reactions are well established.²⁸

It was of some interest that the carbon tetrachloride and chloroform adducts could not be isolated in analytical purity, even upon careful distillation under high vacuum. Dehydrochlorination occurred readily, giving rise to 3-dichloromethylenenorbornadiene (VII and IX) contaminants. The same exocyclic olefins were obtained by alcoholic KOH treatment of the parent compounds. Infrared absorptions at 1668 and 885 cm^{-1} indicated the presence of an exocyclic dichloromethylene group.^{29,30} Ozonolysis yielded phosgene, isolated as *N,N'*-diphenylurea. That the norbornadiene skeleton remained intact during dehydrochlorination was shown by ozonolysis to norbornadieneone.³¹ The steps involved in these structural determinations are summarized in reactions 1–4.

Discussion

The free-radical chain nature of olefin additions has been well substantiated for aldehydes,³² phosphites,³³ perhalomethanes,³⁴ and thiols.^{15,35} Equations 5 through 17 satisfactorily account for all of the products obtained

(27) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 4253 (1948).

(28) For a review, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 278–282.

(29) The strained nature of the exocyclic methylene (1668 cm^{-1}) is reflected in the infrared spectra of methylenecyclopentane (1657 cm^{-1})³⁰ and 2-methylenecyclo[2.2.1]hept-5-ene (1658 cm^{-1}): R. C. Lord and F. A. Miller, *Appl. Spectry.*, **10**, 115 (1956).

(30) H. W. Thompson and P. Tarkington, *Proc. Roy. Soc. (London)*, **A184**, 21 (1945).

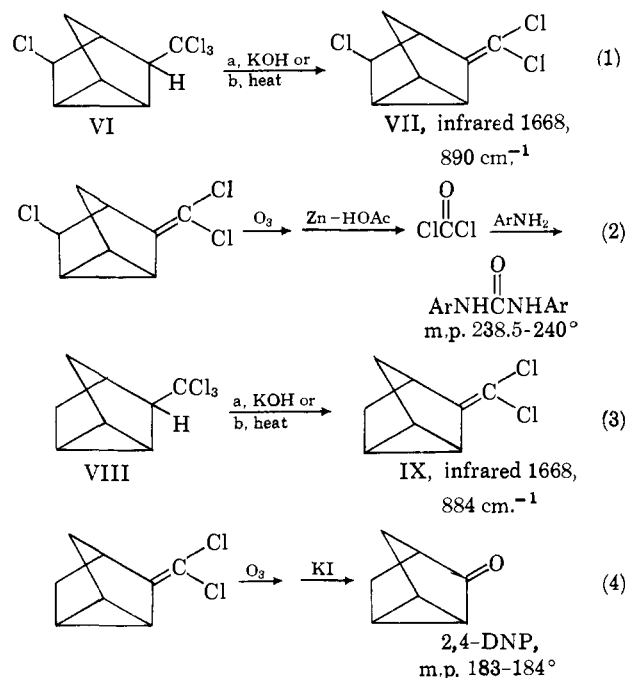
(31) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).

(32) (a) M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949); (b) T. M. Patrick, Jr., *ibid.*, **17**, 1009, 1269 (1952).

(33) (a) W. E. Hanford and R. M. Joyce, U. S. Patent 2,478,390 (August 9, 1949); (b) E. C. Ladd and M. P. Harvey, U. S. Patent 2,664,438 (December 29, 1953); (c) A. R. Stiles and F. F. Rust, U. S. Patent 2,724,718 (November 22, 1955).

(34) C. Walling, ref. 28, pp. 248–250.

(35) (a) M. S. Kharasch, A. T. Read, and F. R. Mayo, *Chem. Ind. (London)*, **57**, 752 (1938); (b) S. O. Jones and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2452 (1938); (c) A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *J. Org. Chem.*, **27**, 2439 (1962), and references therein.



from the reactions involved here. Steps 13 through 17 indicate some of the chain termination possibilities.

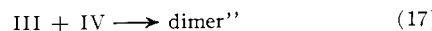
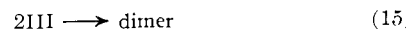
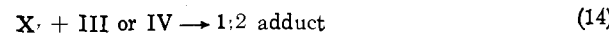
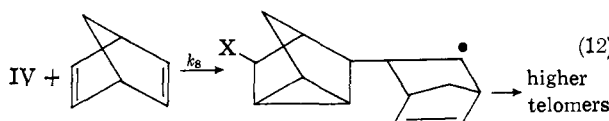
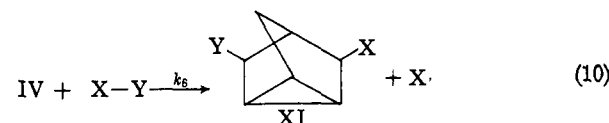
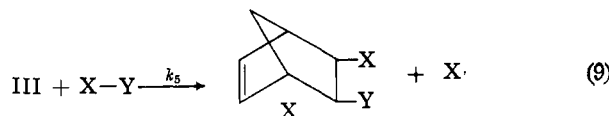
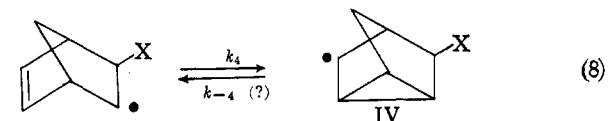
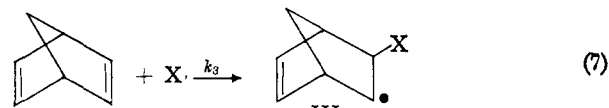
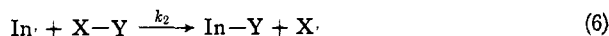


Table II lists the *F*-values³⁶ obtained from the reaction of norbornadiene with a number of the adducts.

(36) J. A. Berson and C. J. Olsen, *J. Am. Chem. Soc.*, **84**, 3178 (1962).

TABLE II
 COMPILATION OF F -VALUES^a

Addend	Diene-peroxide molar ratio	F -Value
CCl ₄	9:1	2.80
CHCl ₃	9:1	2.65
(EtO) ₂ P-H ^b	3:1	2.47
↓ O		
C ₃ H ₇ CHO (1)	6:1	1.32
C ₃ H ₇ CHO (2)	7:1	1.60
C ₃ H ₇ CHO (3)	10:1	2.21
C ₆ H ₁₃ CHO	9:1	2.40

^a F -Value represents moles of product per mole of radicals produced from peroxide; cf. footnote 36. ^b Diene-peroxide solution added dropwise during course of reaction.

Though not a direct measure of chain lengths, these values do indicate that only short kinetic chains are operative in these reactions. It may be noted that the F -values obtained for the butanal addition decrease regularly with increasing peroxide concentration. This is expected, since the higher steady-state concentration of radicals produced from larger amounts of peroxide will enhance the probability of chain termination.

The kinetics of such telomerization reactions, where the addend is present in large excess, can be approximated by the rate expression^{37, 38}

$$-d[M]/dt = k_3[M](R_i/2k_6)^{1/2}$$

The curves for the log of norbornadiene disappearance plotted against time are given in Fig. 2 for the chloroform and butanal addition reactions. It can be seen that, over the period measured, the reaction is first order in diene, as predicted by the rate expression. Short induction periods exist in both reactions.

Chain-transfer constants³⁹ for all addends have been determined; they are compiled in Table III. These

 TABLE III
 CHAIN-TRANSFER CONSTANTS^a

Addend	\bar{P}	C
CCl ₄	1.67	0.20
CHCl ₃	1.78	.17
(EtO) ₂ P-H	2.17	.11
↓ O		
C ₃ H ₇ CHO	2.28	.10
C ₆ H ₁₃ CHO	1.98	.14
C ₆ H ₅ -SH	1.05	19.1

^a Chain-transfer constants have been calculated according to the equation of Mayo,^{39a} $\bar{P} = ([M]/C[S]) + 1$. Here, \bar{P} is the average number of diene units per molecule of product; C is the chain-transfer constant; and $[M]/[S]$ is the average molar ratio of diene to addend.

values are a measure of the propensity of a radical intermediate, such as III or IV, to abstract a hydrogen or halogen atom from the addend (steps 9 + 10) rather than to add to another molecule of substrate (steps 11 + 12). It must be pointed out that the *absolute* values of the transfer constants are not reliable because of the low average molecular weights of the products. Moreover, since the nature of chain termination cannot be accurately assessed, the constants determined here must of necessity represent a lower limit. To the extent that coupling of 3-substituted 5-nortricyclyl radicals occurs (step 16), the

(37) C. Walling, ref. 28, pp. 244-259.

(38) M = norbornadiene concentration and R_i = rate of initiation (steps 5 and 6).

(39) (a) R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, **2**, 328 (1947); (b) W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *J. Am. Chem. Soc.*, **76**, 450 (1954).

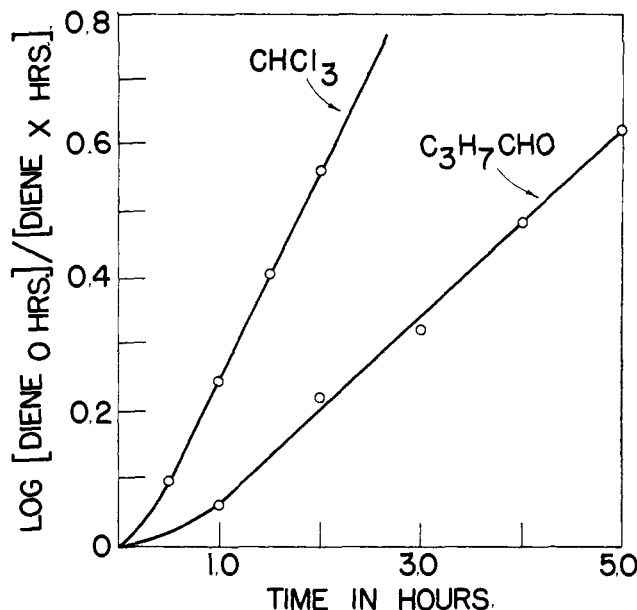


Fig. 2.—Curves of norbornadiene disappearance plotted vs. time for the chloroform and butanal addition reactions.

value of C will appear proportionally low. However, the values are internally consistent and do offer a means of direct, semiquantitative comparison of *relative* chain-transfer rates with different addends.⁴⁰

Thus, it is noted that for the reactions which give *only* nortricyclenes, the corresponding chain-transfer constants appear consistently low. This indicates a slow chain-transfer step and gives some quantitative basis for the postulate that radical rearrangement (step 8) occurs faster than chain transfer (step 9) with k_4 being considerably greater than k_5 and k_6 . The result is that rearrangement to the nortricyclyl radical (IV) competes favorably with chain-transfer by intermediate III. Thiophenol, on the other hand, gives rise to both nortricyclene and norbornene derivatives. As might be expected, its chain transfer constant is markedly higher than any other recorded in this study. This, then, suggests that k_4 and k_5 are of the same order of magnitude when thiophenol is used as the addend, and that, in turn, chain transfer of intermediate III is able to compete with the rearrangement step 8.⁴¹

Nature of the Intermediate.—The question of a nonclassical free-radical analogous to the nonclassical norbornene carbonium ion (I and II) has been discussed by numerous authors.⁴²⁻⁴⁴ Cristol and his co-workers¹⁵ have reported that the ratio of *exo*-5-norbornen-2-yl *p*-tolyl sulfide to 3-nortricyclyl *p*-tolyl sulfide, the products derived from the reaction of *p*-thiocresol with norbornadiene, decreased substantially with decreasing thiol concentration. This was ascribed to the prolonged lifetime of the intermediates III, which thus had more time for rearrangement to IV and less opportunity for chain transfer with *p*-thio-

(40) Known chain-transfer constants for chloroform (0.8), carbon tetrachloride (0.7), aliphatic aldehydes (0.8), and thiols (>16) in radical additions to ethylene indicate a similar order of reactivity: C. Walling, ref. 28, pp. 257, 278, and 319.

(41) The inhibition of radical rearrangements by thiols has been demonstrated by previous workers. Cf. J. Weinstock and S. N. Lewis, *J. Am. Chem. Soc.*, **79**, 6243 (1957); S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

(42) (a) J. A. Berson and W. M. Jones, *J. Am. Chem. Soc.*, **78**, 6045 (1956); (b) J. A. Berson, C. J. Olsen, and J. S. Wallia, *ibid.*, **84**, 3337 (1962); (c) footnote 15 and references 7-9 therein.

(43) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

(44) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

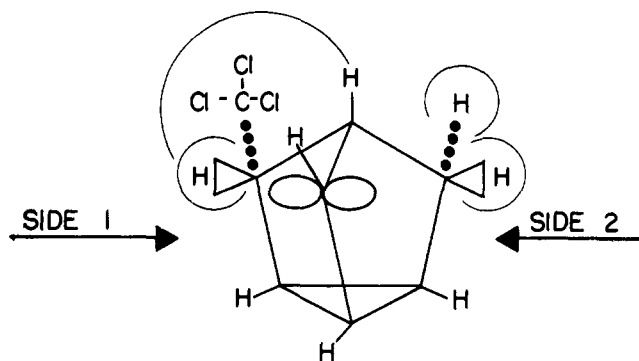


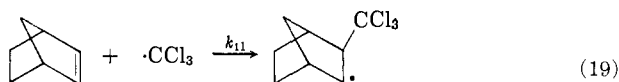
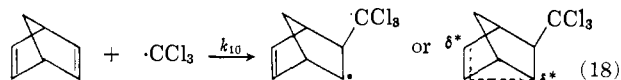
Fig. 3.—The 3-trichloromethyl-5-norbornene radical. Attacks from the two possible sides shown.

cresol.⁴⁵ These workers concluded then that a mesomeric intermediate such as V was not involved, since dilution would not have affected the ratio of products derived from it.

Wilt and Levin,⁴⁴ on the other hand, in a study of the decarbonylation of 5-norbornene-2-carboxaldehyde, found that a fivefold dilution had no effect on the ratio of norbornene and norbornene products. This may be taken as evidence for either a mesomeric intermediate (V) or a rapid equilibrium between III and IV.

Homoconjugation of the sort indicated by V might be expected to lower the energy of the radical addition step and thus substantially enhance the rate over that of systems where such participation in the transition state is not possible.⁴⁶ To test this possibility, a series of reactions was run in which equimolar amounts of norbornadiene and norbornene were allowed to compete for the trichloromethyl radical, generated from chloroform and benzoyl peroxide. Independent experiments showed that H-abstraction by the trichloromethyl radical from either substrate was negligible.⁴⁷

A first-order plot of olefin disappearance *vs.* time afforded two straight lines whose relative slopes were in the ratio of 2.06:1.00. Since the ratio of the slopes is directly proportional to the ratio of the specific



$$\frac{k_{10}}{k_{11}} \propto \frac{\text{1st order slope (18)}}{\text{1st order slope (19)}}$$

rate constants (k_{10}/k_{11}), one may safely conclude that the rate of $\cdot\text{CCl}_3$ addition to norbornadiene is, within experimental error, exactly twice that of addition to norbornene. Thus the effect of the second double bond appears to be strictly additive. This may be cited as evidence against anchimeric assistance involving an entity, such as V.

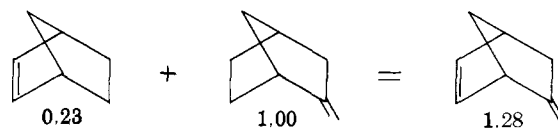
These results are consistent with the recent findings of Huyser and Echeagaray,⁴⁵ who reported that the

(45) Assuming that k_{-4} is negligibly small, the following relationship should be valid if X and XI are derived from different intermediates (III and IV): $X1/X = k_4/k_5[\text{thiol}]$.

(46) Note similar considerations in 5-brosyl-2-norbornene ethanolysis, which involves rate enhancement by charge delocalization of the intermediate carbonium ion (I and II): S. Winstein, H. M. Walborsky, and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).

(47) This is not unexpected, since bridgehead⁴⁸ and methylene⁴⁹ attack of norbornene by radical intermediates is negligible. Moreover, hydrogen abstraction from norbornadiene by methyl radicals occurs only to a very small extent.¹¹

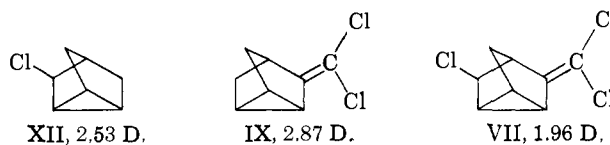
internal double bond in 5-methylene-2-norbornene did not abnormally enhance reactivity of the molecule toward $\cdot\text{CCl}_3$ attack. Rather, they found that the diene reacted as the sum of its isolated double bonds—



further evidence against the existence of a nonclassical radical.

Stereochemistry.—It is well established that attacks on the double bond of norbornene and norbornadiene occur exclusively from the *exo* direction.^{15,18,43} Little is known, however, about the stereochemistry at the 5-position in the 3,5-disubstituted norbornene product. Capillary v.p.c. analysis of the 3-dichloromethylene-5-chloronorbornene obtained in this study showed that only one isomer was present.⁴⁹ This apparent stereospecificity indicates that attack by the intermediate radical was effective from only one direction. The two possibilities are shown schematically in Fig. 3.

In order to ascertain whether the 5-chloro substituent was *exo* or *endo* (with respect to the methylene bridge) and, by implication, whether attack was from side 1 or side 2, we undertook a series of dipole moment studies. The moments of VII, IX, and XII were determined by the method of Guggenheim.⁵⁰ The values obtained are indicated below.



Pertinent angles between each of the possible 5-chloro positions and the 3-dichloromethylene group were calculated. A 61° angle was shown to exist between the *endo*-chloro position and the dichloromethylene entity, and a 138° angle, between the *exo*-chloro position and the dichloromethylene.⁵¹ On this basis, with the measured moments of IX and XII taken as the partial moments of VII, it was possible by vector addition to estimate⁵² the resultant dipoles of the *endo* and *exo* isomers of VII.

Two assumptions were made here. First it was assumed that, to a first approximation, the principal moment of force in compounds IX and XII lay along the line of the substituent-norbornene carbon bond and in that direction. While this cannot precisely be the case, the high degree of symmetry in the norbornene nucleus²² permits such an approximation. Second, it was assumed that classical vector methods could be applied to the nonbisecting moments of force in compound VII. Examination of Dreiding models of this compound indicates that the deviation from a central intersection is small and that any error resulting from such an approximation will not significantly affect the over-all calculation.

The dipole moment of 3-dichloromethylene-*endo*-5-chloronorbornene was calculated to be 4.65 D., while that of the *exo* isomer was estimated at 1.96 D.

(48) F. S. Huyser and G. Echeagaray, *J. Org. Chem.*, **27**, 429 (1962).

(49) Isolation of identical products from base-catalyzed and thermal dehydrochlorination of VI rules out the possibility of base-induced epimerization at the 5-chloroposition.

(50) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

(51) Throughout all calculations, the Lippincott²² model of norbornene (Fig. 1) was employed. The bond angles assigned were those which imposed minimum strain on the molecule.

(52) C. P. Smyth in A. Weissberger, "Technique of Organic Chemistry," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1949, pp. 1611-1617.

Thus, if the δ -chloro group is in an *endo* position, the over-all moment of the molecule should be enhanced. Conversely, if the δ -chloro group is *exo* to the methylene bridge, the resultant moment should be reduced. This becomes apparent if the molecule is viewed from its top (directly down the bridgehead carbon-hydrogen bond). Such a projection is shown in Fig. 4.

The actual dipole moment of VII was experimentally found to be 1.96 D., identical with the value calculated for the *exo* isomer. Such remarkable agreement must be considered fortuitous and is certainly far better than the experimental technique warrants. To the extent that the nortricyclic nucleus makes any significant vectorial contribution to the dipole moment of the molecule, the angle between the partial moments and, therefore, the calculated moment of VII will be altered somewhat. It might be expected, however, that such an alteration would be a relatively small one.

From these results, then, it may be safely concluded that the stereochemistry of VII is *exo* with respect to the methylene bridge (compound VIIb). By inference, then, one may conclude that a real steric effect is exerted by the trichloromethyl group in the chain-transfer step. The ease of approach from side 2 (Fig. 3) may be contrasted to the apparent difficulty encountered in the approach from the hindered 1 side.

Experimental

Reagents.—Norbornadiene (Shell Chemicals) was redistilled (b.p. 89–89.5°, n_D^{25} 1.4684) and stored in a tightly stoppered container under nitrogen. Norbornene (Shell Chemicals) was similarly purified (b.p. 90–91°). The following reagents were redistilled shortly before use: butanal (Matheson, b.p. 74–75°, n_D^{25} 1.3774), 2-methylpropanal (Matheson, b.p. 63–64°, n_D^{25} 1.3709), heptanal (Matheson, b.p. 50–51° at 16 mm.), and diethyl phosphite (Matheson, b.p. 69–70° at 10 mm.). *t*-Butyl peroxide (Eastman White Label), benzoyl peroxide (Eastman White Label), thiophenol (Matheson), carbon tetrachloride, and chloroform were used without further purification. All melting points and boiling points are uncorrected unless otherwise specified.

General Procedure A.—Addend, substrate, and peroxide were placed together in a 300-ml. of 1-l. round-bottom flask, which was equipped with (a) a sintered glass diffuser for nitrogen ebullition, (b) a thermocouple well, (c) a small outlet tube covered with a rubber septum, for periodic hypodermic sampling, and (d) a brine-cooled reflux condenser. Nitrogen was bubbled through the solution for 30 min. prior to heating. Then the reaction flask was lowered into an oil bath, which was maintained at a temperature about 5° above that of the peroxide decomposition point. A gentle nitrogen purge was continued for the duration of the reaction. In most instances, the reaction was followed by means of v.p.c. analysis.

General Procedure B.—All of the addend and small portions of the total substrate and peroxide were placed in the reaction flask, and the system was brought to reaction temperature as previously described. The remainder of the substrate and peroxide was then added dropwise to the reaction mixture throughout the course of the reaction.

N.m.r. Analysis of Products.—Nuclear magnetic resonance studies of all adducts enabled chemical shift assignments to be made to the protons on carbon atoms 3, 4, and 5 (see Fig. 1). In instances where electron-withdrawing groups were present in the 3-position or both the 3- and 5-positions, notable paramagnetic shifts were observed for all neighboring protons. Such deshielding was perhaps most apparent with the bridgehead (C-4) proton. In the unsubstituted nortricyclic molecule, this proton exhibited a resonance at 8.09 τ .⁵³ With the diethyl phosphonate group on the carbon α to the C-4 proton, the signal shifted downfield slightly, to 7.97 τ . A more pronounced deshielding effect (7.65 τ) resulted when a trichloromethyl group was present in the 3-position. 3-Trichloromethyl 5-chloro disubstitution exerted a still stronger effect, lowering the resonance to 7.50 τ . The C-3 proton exhibited a similar paramagnetic shift from its unsubstituted value of 8.78 τ ⁵³ with increasing electronegativity of C-3 substituents (see Table V).⁵⁴ The

(53) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

(54) Except where indicated, the signals attributable to C-3 and C-4 protons appear as broadened singlets (coupling constants less than 1 c.p.s. in all cases). The lack of coupling with protons on C-1, C-2, C-5, and C-7 indicates that unfavorable dihedral angles may exist between these and the protons attached to C-3 and C-4. Calculation of these pertinent angles,

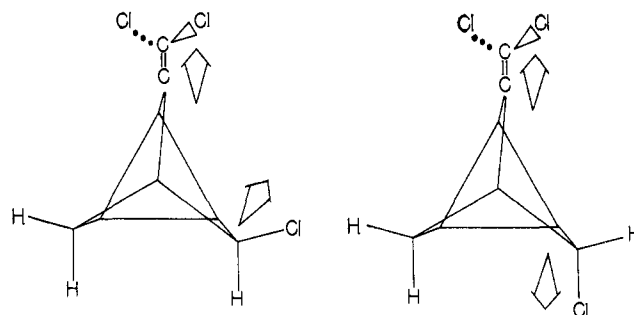


Fig. 4.—Top projections of nortricyclic, obtained by viewing directly down the bridgehead methine (C-4). Arrows indicate the approximate direction of the dipoles in the *endo* (VIIa) and *exo* (VIIb) isomers.

chloro-adjacent proton in compounds IX and X gives a signal at 5.96 τ , a value consistent with previous results.^{19,55}

Addition of Butanal to Norbornadiene.—Butanal (115 g., 1.6 moles), norbornadiene (36.8 g., 0.40 mole), and benzoyl peroxide (15.9 g., 0.065 mole) were brought into reaction at 80 \pm 2° for 35.5 hr., as described in procedure A. Vapor phase chromatographic analysis^{56a} of the reaction mixture revealed four peaks, A–D, in addition to the starting material. The products were separated by careful fractionation on a 36-in. Nester and Faust spinning-band column. All materials assigned a structure were shown to be homogeneous by v.p.c. (A) 3-Propylnortricyclicene (1.5 g., 0.011 mole, 2.8% yield) was collected as a colorless liquid at 55–60° at 10 mm. An analytical sample (b.p. 131–133°, n_D^{20} 1.4216) was obtained by means of preparative scale v.p.c.^{56b}

TABLE IV
INFRARED SPECTRAL DATA

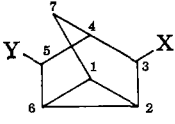
Y		X	Cyclopropyl C-H, cm. ⁻¹	Nortricyclic, cm. ⁻¹	Characteristic doublets, cm. ⁻¹		Functional groups, cm. ⁻¹
—CCl ₃	—H		3040	803	1457	1303	C—Cl, 823, 780, 746
—CCl ₂	—Cl		3038	803	1458	1303	C—Cl, 828, 780, 753
=C	—Cl		3038	790	1455	1292	>C=CCl ₂ , 1668, 890
=C	—H		3032	790	1450	1300	>C=CCl ₂ , 1668, 884
η -C ₂ H ₅	—H		3040	804	1458	1300	...
η -C ₃ H ₇	—H		3040	800	1458	1300	...
O	—C=O		3045	802	1458	1306	>C=O, 1715
O	—C=O		3040	807	1456	1300	>C=O, 1700
O	—P(OEt) ₂		3040	802	1458	1300	P \rightarrow O, 1240 ^a P—O—C, 1040 ^b
—S—Ar	—H		3045	803	1455	1290	Ar—H, 3005, 719, and 694

^a L. J. Bellamy and L. Beecher, *J. Chem. Soc.*, 475, 1701 (1952); 728 (1953). ^b L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

utilizing Lippincott's model and bond angles,²² lends support to this explanation. The dihedral angle between the protons on C-3 and C-4 was estimated to be 80°, while that between C-2 and C-3 was found to approach 64°.

(55) The C-3 proton in 3-chloronortricyclicene exhibits an absorption at 6.12 τ . See also L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 54.

(56) (a) Ten-foot columns of Carbowax 4000 and Carbowax 6000 on Chromosorb P and W, in an Aerograph Model A-110-C with Brown recorder and integrator, were used for all analytical work. (b) All preparative scale v.p.c. work was carried out on a Nester and Faust preparative gas chromatograph, employing a 5-ft. by 0.75-in. column of Carbowax 6000 on Chromosorb P.

TABLE V
 N.M.R. SPECTRAL DATA^a


Y	X	C-3 proton, τ	C-4 proton (bridge-head), τ	C-5 proton, τ
Cl	$=\text{CCl}_2$..	7.20	5.97
H	$=\text{CCl}_2$..	7.32	
Cl	CCl_3	7.22	7.50	6.05
H	CCl_3	7.28	7.65	8.63 (C-5 and C-7 protons)
H	$\text{PO}(\text{OEt})_2$	8.30 (doublet)	7.97	8.80 (multiplet, C-5 and C-7 protons)

^a Nuclear magnetic resonance spectra were recorded with a Varian A-60, using carbon tetrachloride as solvent, with tetramethylsilane as an internal reference. Chemical shifts are recorded in τ -values [G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)].

Anal. Calcd. for $\text{C}_{10}\text{H}_{16}$: C, 88.15; H, 11.85; parent mass, 136. Found: C, 87.82; H, 11.62; parent mass, 136.

(B) 4-Heptanol (1.24 g., 0.011 mole, 1.4% yield) was obtained in a fraction boiling at 67–70° at 10 mm. and was separated on the preparative scale v.p.c. Its infrared spectrum exhibited a strong O–H band (3400 cm^{-1}).

Anal. Calcd. for $\text{C}_7\text{H}_{16}\text{O}$: parent mass, 116. Found: parent mass, 116.

The 3,5-dinitrobenzoate was prepared. Recrystallization from aqueous ethanol afforded white plates which melted at 64–65° (lit.⁵⁷ m.p. 64°).

(C) Butanoic acid (1.45 g., 0.017 mole, 1.0% yield) was obtained as a colorless liquid boiling at 88–89° at 10 mm. Its physical properties and infrared spectrum were identical with those of an authentic sample.

(D) 3-Butanoylnorbornadiene (28 g., 0.171 mole, 42.7% yield) was collected at 98–101° at 10 mm. Redistillation yielded an analytical sample (b.p. 75–77° at 1.5 mm., n_D^{20} 1.4736).

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.48; H, 9.76; parent mass, 164. Found: C, 80.18; H, 9.71; parent mass, 164.

A 2,4-dinitrophenylhydrazone was prepared. After two recrystallizations from 95% ethanol and extensive drying, the light orange needles melted at 89–91°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{O}_4\text{N}_4$: C, 59.48; H, 5.54. Found: C, 59.56; H, 5.83.

The semicarbazone of 3-butanoylnorbornadiene was also prepared. Two recrystallizations from very dilute ethanol and extensive drying *in vacuo* afforded white needles which melted at 132–133°.

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{ON}_3$: C, 65.15; H, 8.60; N, 19.00. Found: C, 65.17; H, 8.50; N, 19.16.

Following the 3-butanoylnorbornadiene fraction, benzoic acid (15.7 g., 0.129 mole, 99% of theoretical) sublimed into the head of the column. The crystals, after resublimation, melted at 120–121° (lit. m.p. 121–122°). Admixture with an authentic sample caused no depression of melting point (121–122°). A dark, viscous mixture of higher telomers (mol. wt., 375) remained as the distillation residue. Pertinent infrared maxima were recorded at 3040, 2950, 1710, 1615, 807, and 712 cm^{-1} .

Further butanal additions were made according to procedure B. All analyses were made solely by v.p.c., with *p*-dichlorobenzene employed as an internal standard. A sample of *p*-dichlorobenzene (0.0687 g., 4.6×10^{-4} mole) was carefully weighed out and dissolved in a sample of authentic 3-butanoylnorbornadiene (0.1712 g., 1.04×10^{-3} mole). The calculated molar ratio 31:69 was compared with the area ratio determined by v.p.c. (25:75), and a correction factor of 0.742 was calculated for converting the observed 3-butanoylnorbornadiene/*p*-dichlorobenzene molar ratio to the true value. The results are summarized in Table I.

Addition of Diethyl Phosphite to Norbornadiene.—A solution of norbornadiene (58 g., 0.63 mole) and *t*-butyl peroxide (9.45 g., 0.064 mole) was added to a heated (137 ± 7°), stirred mixture of diethyl phosphite (138 g., 1.00 mole), norbornadiene (11 g., 0.12 mole), and *t*-butyl peroxide (2.0 g., 0.014 mole) over a period of 26 hr., as outlined in procedure B. Vapor phase chromatographic analysis indicated that only one product (with the exception of nonvolatile telomers) had been formed. After the unreacted diethyl phosphite and peroxide decomposition products (acetone

and *t*-butyl alcohol) had been rapidly distilled away, fractionation was continued on a 9-in., vacuum-jacketed Vigreux column. After a small forerun (7.0 g., b.p. 81–100° at 1 mm.), 3-norbornadiene diethyl phosphonate (88.58 g., 0.385 mole, 51.4% yield) was collected in thirteen fractions (b.p. 100–101° at 1 mm., 95–96° at 0.5 mm, n_D^{20} 1.4677–1.4689).

The product was homogeneous to v.p.c. Nuclear magnetic resonance analysis showed a quintet,⁵⁸ centered at 5.95 τ (methylene protons in ethoxy group); two broadened singlets (2 protons) at 7.97 and 8.08 τ (C-4 and C-2); a doublet (12 c.p.s., 1 proton) centered at 8.30 τ (C-3); a triplet (6 protons) centered at 8.73 τ (methyl protons in ethoxy groups); and an unresolved multiplet (6 protons) centered at 8.8 τ .

Anal. Calcd. for $\text{C}_{11}\text{H}_{19}\text{O}_5\text{P}$: C, 57.37; H, 8.26; P, 13.47; mol. wt., 230. Found: C, 56.96; H, 8.27; P, 13.36; mol. wt., 225.

A viscous, amber residue, consisting of higher telomers (average molecular weight, 391), remained in the distillation flask. In the infrared spectrum, an absorption at 712 cm^{-1} appeared, in addition to those maxima exhibited by the 1:1 adduct.

Addition of Carbon Tetrachloride to Norbornadiene.—As outlined in procedure A, carbon tetrachloride (568 g., 4.00 moles), norbornadiene (92 g., 1.00 mole), and benzoyl peroxide (29 g., 0.12 mole) were brought into reaction at 78 ± 2° for 6.25 hr. Unreacted CCl_4 and peroxide-derived chlorobenzene were removed by distillation *in vacuo*. A portion of hexachloroethane (23 g., sublimation point 185–186°) then sublimed onto the column head. Continued fractionation on the 36-in. spinning-band column yielded: (A) 3-Dichloromethylene-5-chloronorbornadiene (6.50 g., 0.031 mole, b.p. 87–95° at 1 mm.) was characterized by comparison with a sample obtained later by dehydrochlorination of the adduct. (B) 3-Trichloromethyl-5-chloronorbornadiene (157.5 g., 67.3% yield, b.p. 88.5–93° at 0.6 mm., n_D^{20} 1.5391–1.5407) was collected in 22 fractions; v.p.c. analysis indicated that all fractions were contaminated by VII. Careful refractionation effected no separation; varying amounts of VII remained in all cuts. (C) An intractable, dark residue, composed in part of higher telomers (average molecular weight 434), remained in the distillation flask.

The Dehydrochlorination of VI.—Compound VI (41.9 g., 0.17 mole) and a solution of potassium hydroxide (11.2 g., 0.20 mole) in absolute ethanol (100 ml.) were stirred together under reflux for 2 hr. At the end of that time, a copious amount of potassium chloride (10.5 g., 71% of theoretical) had precipitated from the solution. Distillation on the 8.5-in., vacuum-jacketed Vigreux column yielded 3-dichloromethylene-5-chloronorbornadiene (21.43 g., 0.103 mole, 60.2% yield, b.p. 78.5–80° at 1 mm., n_D^{20} 1.5510–1.5515, homogeneous to v.p.c.).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{Cl}_2$: C, 45.82; H, 3.34; Cl, 50.83; mol. wt., 210. Found: C, 46.17; H, 3.34; Cl, 50.87; mol. wt., 218.

3-Dichloromethylene-5-chloronorbornadiene was also obtained by pyrolysis of the 1:1 adduct VI. Compound VI (4.09 g., 0.0166 mole) was heated to 170–180° under a continuous N_2 purge for 2.5 hr. Infrared spectroscopy and v.p.c. analysis indicated that nearly all of VI had been converted to the dehydrochlorinated product VII. In both cases, a dark, viscous residue remained in the flask after distillation.

Addition of Chloroform to Norbornadiene.—Chloroform (718 g., 6.00 moles), norbornadiene (138 g., 1.50 moles), and benzoyl peroxide (41 g., 0.17 mole) in chlorobenzene (169 g., 1.50 moles) were brought into reaction at 80 ± 3° for 7.5 hr., as described in procedure A. The chlorobenzene and unreacted chloroform were then removed by reduced-pressure distillation. Hexachloroethane was sublimed from the reaction mixture. Continued fractionation, on a 36-in. spinning-band column, gave 3-trichloromethylnorbornadiene (191 g., 0.90 mole, 60% yield, b.p. 61–64° at 1 mm., n_D^{20} 1.5213–1.5218). All cuts were shown by v.p.c. to be contaminated with 3-dichloromethylnorbornadiene (IX). An intractable, dark residue, composed of higher telomers (average molecular weight 391), remained in the distillation flask. An infrared spectrum of the residue exhibited characteristic absorptions at 707, 740–780, and 810 cm^{-1} .

The Dehydrochlorination of VIII.—Treatment of VIII (37.47 g., 0.177 mole) with potassium hydroxide (9.9 g., 0.177 mole) in absolute ethanol (65 ml.) under reflux for 2.5 hr. afforded an abundant white precipitate of potassium chloride. Distillation under reduced pressure on the 36-in. spinning-band column gave 3-dichloromethylnorbornadiene (12.51 g., 0.072 mole, 41% yield, b.p. 72.5–73.5° at 4 mm., n_D^{20} 1.5339–1.5344, homogeneous to v.p.c.).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{Cl}_2$: C, 54.86; H, 4.57; Cl, 40.57; mol. wt., 175. Found: C, 54.91; H, 4.83; Cl, 40.58; mol. wt., 179.

(58) The coupling constant of $\text{P}-\text{CH}_2$ is the same as the coupling constant of CH_3-CH_2 ; thus the signal appears as a quintet. Cf. "Manufacturing Chemists Association Research Project, NMR Spectral Data," Texas A. & M., Dec. 31, 1960, Serial 91.

(57) H. Adkins, R. Connor, and H. Cramer, *J. Am. Chem. Soc.*, **52**, 5192 (1930).

A similar dehydrochlorination of VIII (51.26 g., 0.242 mole) resulted in a 55% yield of isolable IX (23.32 g., 0.133 mole). In each case, a dark, resinous residue made up the remainder of the reaction product.

Ozonolysis of 3-Dichloromethylene-5-chloronortricyclene.⁵⁹—A Welsbach T-23 ozonator was used for the ozonolysis. A flowmeter, connected in series after the reaction flask, indicated the approximate flow rate of ozone-containing oxygen. A trap filled with KI solution served to indicate when the reaction was complete.

Compound VII (3.00 g., 0.0143 mole) was taken up in ethyl acetate (150 ml.), cooled to -10° , and ozonized with a nearly quantitative amount of O_3 (0.015 mole). Aniline (15 ml.) was then added, and a copious precipitate formed immediately. The reaction mixture was allowed to stand for 4.5 hr. at -10° , and then for 21.5 hr. at room temperature. Reduction was carried out with zinc dust (2.5 g.) and acetic acid (25 ml.). The mixture was then transferred to a separatory funnel and washed successively with water (50 ml.), 5% HCl (25 ml.), water (25 ml.), 5% NaOH (25 ml.), and finally again with water (25 ml.). The brownish white solid that remained in the aqueous layer was collected by filtration and sublimed under high vacuum. The white sublimate was twice resublimed to yield white needles which melted at $238.5\text{--}240^{\circ}$. A mixture with an authentic sample of N,N'-diphenylurea (m.p. $237\text{--}238^{\circ}$)⁶⁰ resulted in no depression of the melting point ($237\text{--}238^{\circ}$).

Ozonolysis of 3-Dichloromethylenenortricyclene.—The ozonolysis of 3-dichloromethylenenortricyclene was carried out in a similar manner. Compound IX (3.22 g., 0.0184 mole) was dissolved in methanol (30 ml.) and subjected to ozonolysis at -78° for 20 min. The ozone uptake was nearly quantitative (18.4 mmoles). Reduction was carried out with KI in such excess that the reaction was complete in a few minutes. The iodine formed was titrated with sodium thiosulfate. The methanol was then stripped off on a Rinco rotary evaporator, and the remaining two-layer system was thrice extracted with ether. The combined ether extracts were dried over sodium sulfate, and evaporated to a clear, oily residue. A portion of the residue was added to acidic 2,4-dinitrophenylhydrazine. A light orange precipitate formed immediately and was recrystallized five times from absolute ethanol to a constant melting point of $183\text{--}184^{\circ}$.

Anal. Calcd. for $C_{13}H_{12}N_4O_4$: C, 54.16; H, 4.16; N, 19.44. Found: C, 54.09; H, 4.05; N, 19.36.

An authentic sample of 3-nortricyclenone 2,4-dinitrophenylhydrazone was prepared by means of chromic acid oxidation of 3-nortricyclenol (m.p. $108\text{--}109^{\circ}$).^{60,61} The light orange needles were recrystallized three times from absolute ethanol and dried extensively. They melted at $183\text{--}184^{\circ}$ (lit.⁶² m.p. $184\text{--}185^{\circ}$). The mixture melting point of the ozonolysis product and the authentic sample was undepressed ($182\text{--}183^{\circ}$).

A second ozonolysis of IX (2.50 g., 0.0143 mole) was carried out in methylene chloride (150 ml.) at -10° . Addition of aniline (12 ml.) and work-up in the manner described previously yielded N,N'-diphenylurea (m.p. $236.5\text{--}238^{\circ}$,⁶⁰ m.m.p. $237\text{--}238^{\circ}$).

Addition of Heptanal to Norbornadiene.—Norbornadiene (29 g., 0.315 mole), heptanal (144 g., 1.26 moles), and benzoyl peroxide (8.1 g., 0.036 mole) were brought into reaction at $81 \pm 2^{\circ}$ for 11.75 hr., as outlined in procedure A; v.p.c. analysis indicated the presence of three products. Fractionation of the reaction mixture was carried out on the 36-in. spinning-band column. After the unreacted heptanal was removed, two of the three products were isolated and identified.

(A) 3-*n*-Hexylnortricyclene (3.5 g., 66% pure, or 2.3 g., 0.015 mole, 4.8% yield, b.p. $84\text{--}90^{\circ}$ at 2 mm.) was collected in an early fraction. An analytical sample (b.p. 229° , n_D^{20} 1.4623) was obtained by means of preparative scale v.p.c.

Anal. Calcd. for $C_{13}H_{22}$: C, 87.64; H, 12.36; parent mass, 178. Found: C, 87.62; H, 12.34; parent mass, 178.

Next, benzoic acid (m.p. and m.m.p. $121\text{--}122^{\circ}$) sublimed into the distillation head (8.0 g., 0.065 mole, 90% of theoretical).

(B) 3-Heptanoylnortricyclene (30.4 g., 0.148 mole, 47.7% yield) was obtained as a colorless liquid at $137\text{--}138^{\circ}$ at 6.5 mm. An analytical sample was obtained by collecting numerous samples from the gas outlet of an Aerograph Model A-110-C gas chromatography unit (10-ft. column of Carbowax 6000 on Chromosorb W, 225°).

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.55; H, 10.68. Found: C, 81.06; H, 10.60.

The oxime of 3-heptanoylnortricyclene was prepared. After two recrystallizations from aqueous methanol and extensive drying, it melted at $51.5\text{--}53^{\circ}$.

(59) Ozonolyses were kindly carried out by Dr. C. E. Stehr of these laboratories.

(60) A. Sonn, *Ber.*, **47**, 2440 (1914).

(61) A sample of 3-nortricyclenol was generously furnished by Mr. P. S. Starcher of these laboratories.

(62) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).

Anal. Calcd. for $C_{14}H_{22}ON$: N, 6.33. Found: N, 6.24.

A dark viscous residue, composed of higher telomers (average molecular weight 394), remained in the distillation flask. The infrared spectrum of the telomeric mixture exhibited characteristic maxima at 3040, 2940, 2840, 1702, 804, and 712 cm^{-1} .

Addition of Thiophenol to Norbornadiene.—Thiophenol (110 g., 1.00 mole) and norbornadiene (92 g., 1.00 mole) were added dropwise at identical rates to a 500-ml. round-bottom flask, which was equipped with a magnetic stirrer and a reflux condenser, and which was partially immersed in an ice bath. Addition was complete in 30 min. The reaction was extremely vigorous and continued at reflux for some time after both reagents had been added. The mixture was allowed to stand overnight. Distillation yielded a small forerun of thiophenol, then a single fraction (b.p. 116° at 2.5 mm., n_D^{20} 1.5909, 183 g., 0.905 mole, 90.5% yield) of 1:1 adduct. A viscous gold residue (12 g.), composed of higher telomers (average molecular weight 277) remained.

Infrared spectral analysis indicated that the 1:1 adduct was a mixture of norbornene and nortricyclene derivatives (maxima at 1568, 807, and 703 cm^{-1}). Quantitative hydrogenation measurements indicated that the mixture was composed of 80% 3-nortricyclenyl phenyl sulfide and 20% 5-norbornen-2-yl phenyl sulfide; n.m.r. spectroscopy showed, from comparison of olefinic proton areas (3.90 τ) with total phenyl proton areas (2.74 τ), that the mixture of nortricyclene and norbornene derivatives existed in a 77.5:22.5 ratio. An average value of 79% 3-nortricyclenyl phenyl sulfide and 21% 5-norbornen-2-yl phenyl sulfide was assigned to the mixture.

In order to separate 3-nortricyclenyl phenyl sulfide from the mixture, a second mole of thiophenol was added to 5-norbornen-2-yl phenyl sulfide, thus removing it as an isomeric contaminant. A portion of the mixture (150 g.) and thiophenol (30 g.) were stirred together at room temperature for 4 days, after which time no trace of the norbornene derivative was detectable by v.p.c. Fractionation yielded 3-nortricyclenyl phenyl sulfide (b.p. $115\text{--}116^{\circ}$ at 1 mm., 138° at 4 mm., n_D^{20} 1.5936); n.m.r. spectroscopy revealed a multiplet centered at 2.71 (five phenyl protons), a broadened singlet at 6.86 (C-3 proton), an overlapping pattern centered at 8.03 (C-2 and C-4 protons), and a multiplet centered at 8.77 (presumably C-1, C-5, C-6, and C-7 protons).

Anal. Calcd. for $C_{13}H_{14}S$: C, 77.21; H, 6.89. Found: C, 77.22; H, 6.93.

The sulfoxide was prepared by peracetic acid oxidation in accordance with a standard procedure.¹⁵ Twice recrystallized from petroleum ether ($30\text{--}60^{\circ}$), it melted at $88.5\text{--}90^{\circ}$. All infrared maxima (sulfoxide at 1037 cm^{-1} ⁶³ and nortricyclene at 1300 and 803 cm^{-1}) were consistent with the structure.

Anal. Calcd. for $C_{13}H_{14}OS$: C, 71.56; H, 6.42; S, 14.68. Found: C, 71.50; H, 6.33; S, 14.33.

5-Norbornen-2-yl phenyl sulfide was separated from the original mixture and collected by means of analytical scale gas chromatography (10-ft. column of Carbowax 6000 on Chromosorb W, at 225°). Its infrared spectrum (1562 and 704 cm^{-1}) and n.m.r. spectrum (multiplet centered at 3.91 τ , C-5, C-6; multiplet centered at 2.74 τ , phenyl protons; and broadened singlet at 7.05 τ , C-2) are consistent with the assigned structure.

Anal. Calcd. for $C_{13}H_{14}S$: C, 77.21; H, 6.89. Found: C, 77.17; H, 6.89.

Competitive Reaction of Norbornadiene and Norbornene for the Trichloromethyl Radical.—The following reagents were carefully weighed into a reaction flask (described in general procedure A): norbornadiene (11.50 g., 0.125 mole), norbornene (11.75 g., 0.125 mole), chlorobenzene (28.2 g., 0.25 mole), benzene (9.75 g., 0.125 mole), chloroform (119.5 g., 1.00 mole), and benzoyl peroxide (3.39 g., 0.014 mole). Benzene served as an internal standard in v.p.c. analysis for following norbornadiene and norbornene disappearance. Relative thermal conductivities of the three were determined by carefully weighing samples of each into a common solution, then comparing the calculated mole percentages with the area percentages obtained by v.p.c. A 20-ft. column of Apiezon L (83°) readily separated chloroform, benzene, norbornadiene, and norbornene.

The reaction system was flushed with predried nitrogen for 30 min. and then immersed in an oil bath, which had been previously heated to 85° . The reaction system, under these conditions, attained a temperature of $73 \pm 0.5^{\circ}$, which it held for the duration of the 2.5-hr. reaction period. Periodic samples were withdrawn by needle and syringe for v.p.c. analysis. Nearly all of the norbornadiene had reacted in 2.5 hr.

The plot of $\log [\text{olefin } 0 \text{ hr.}] / [\text{olefin } X \text{ hr.}]$ vs. time indicated that the reaction was first order with respect to each olefin over the time 0.25–2.0 hr. An induction period was operative from

(63) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

Time, (hr.)	$\log \frac{[\text{norbornadiene } 0 \text{ hr.}]}{[\text{norbornadiene } X \text{ hr.}]}$	$\log \frac{[\text{norbornene } 0 \text{ hr.}]}{[\text{norbornene } X \text{ hr.}]}$
0.5	0.097	0.080
1.0	.246	.155
1.5	.406	.230
2.0	.563	.310
2.5	.823	.436

0.0–0.25 hr. The ratio of the respective slopes was used to determine the relative rates of addition.

$$\frac{k_{\text{diene}}}{k_{\text{monoene}}} = \frac{0.316}{0.153} = 2.06$$

The possibility of hydrogen abstraction by a radical species rather than addition was tested in an independent experiment in which carbon tetrachloride was used as the source of trichloromethyl radicals. In this instance, any hydrogen-abstraction from bridgehead or ring methylene position of norbornene or norbornadiene would result in the formation of chloroform, which would in turn be detected by v.p.c. analysis. Moreover, H-abstraction by a phenyl radical (derived from benzoyl peroxide) would give rise to benzene, also detectable by v.p.c. A 10-ft. column of Carbowax 6000 on Chromosorb W, operated at 70°, was shown to be capable of separating carbon tetrachloride, benzene, and chloroform (eluted in that order). In no

instance, even after considerable reaction time, was any chloroform or benzene detected.

3-Chloronorbornene.—3-Norbornene⁶¹ (56 g., 0.509 mole) and thionyl chloride (121 g., 1.11 moles) were stirred together for 15 min. at room temperature, then heated to 95°, with continued stirring, for 3 hr. Distillation yielded unreacted thionyl chloride and 3-chloronorbornene (b.p. 55–57° at 12 mm., n_D^{20} 1.4979, infrared spectrum consistent with structure), which was shown to be homogeneous by v.p.c.

Anal. Calcd. for C_7H_9Cl : C, 65.37; H, 7.00. Found: C, 65.69; H, 6.99.

Dipole Moment Determinations.—The method of Guggenheim⁶⁰ was employed in obtaining dipole moments of compounds VII, IX, and XII. Solutions of 2–13% in benzene were prepared for each of these compounds. Refractive indices were measured on an Abbe refractometer, Model G (Carl Zeiss) at 25°. Dielectric constants were determined with a General Radio 716 C capacitance bridge, employing a frequency of 1 Kc. at 25°.⁶⁴

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The Nuclear Magnetic Resonance Spectra and Stereochemistry of Substituted Bornanes¹

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Correlations between n.m.r. spectra and *exo/endo* isomerism in substituted bornanes are presented. Some of the features of the n.m.r. spectra which are sensitive to stereoconfiguration are the chemical shift of the methyne proton on the same carbon as the substituent and the multiplet structure of this α -methyne proton peak. Calculations have been made to arrive at reasonable mechanisms for the change of the multiplet structure with stereoconfiguration.

Nuclear magnetic resonance has been shown to be useful in the determination of stereoconfiguration in several rigid ring systems—sugars,² steroids,³ nucleotides,⁴ and bicyclo[2.1.1]hexane derivatives.⁵ We wish to present here the unique stereochemical correlations in the n.m.r. spectra of substituted bornanes. N.m.r. spectra have been reported for some bicyclo[2.2.1]heptane compounds closely related to the substituted bornanes: by Kumler, *et al.*,⁶ and by Anet.⁷ In all of the work published, there are differences in the spectra of the stereoisomers for 2- and 3-substituted bicyclo[2.2.1]heptanes. Kumler, *et al.*, found that the position of the n.m.r. peak of the proton on the same carbon as the chlorine in *exo*-2-chlorocamphor is higher by 0.48 p.p.m. than the resonance for the corresponding *endo*-2-chlorocamphor. Anet has found that the spin coupling constants in α -methyne protons⁸ of the four 2,3-bornane diol stereoisomers are consistent with Karplus' theory⁹ relating the spin coupling constant of protons on adjacent singly bound carbons to the dihedral angle of the two C–C–H bonds. He also found that long range spin coupling constants of ~ 1 c.p.s. may appear when the α -methyne proton is *exo*—they did not appear for the corresponding *endo*- α -methyne

proton. In our work the n.m.r. spectra of some twenty-one well characterized substituted bornanes are reported.¹⁰ It is felt that enough compounds have now been examined so that the spectra/structure correlations will have general significance.

Chemical Shifts in Substituted Bornanes

Assignment of N.m.r. Peaks.—With the exception of the proton on the same carbon as the substituent R (and, of course, any protons which may be in R), all of the proton resonance peaks for the substituted bornanes are found at 7.0–9.5 τ . The methylene and angular protons appear as a complicated band with considerable structure throughout this region; the methyl groups appear as sharp peaks. The resonances of the protons in the substituent R may be easily assigned from previous work on the resonance positions of such groups.^{11,12}

Chemical Shifts of the Methyl Groups.—Kumler, Shoolery, and Brucher⁶ have proposed that the position of the methyl peaks might be a test of configuration for the group substituted at the 2-position on the [2.2.1]-bicycloheptane ring of the chlorocamphors. Striking differences of the methyl positions in the substituted bornanes have been observed in this study between *exo* and *endo* substitution at the 2-position. For example, in Fig. 1 it is seen that the methyl peaks of borneol (I) are superimposed. The methyl peaks of isoborneol (II) are separate. However in a perusal of the other spectra, no clear pattern which may be

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