better than 5%. After chlorination, the products were determined by g.l.p.c. as described above. Since the extent of conversion of either A or B was always <10%, the relative reactivities were determined from the equation

$$\frac{\text{relative reactivity of B}}{\text{relative reactivity of A}} = \frac{(\text{products from B})(A_0)}{(\text{products from A})(B_0)}$$

Individual runs are given in Table IV; mean values were used to construct column 1 of Table V.

Chlorination Studies of Unsaturated Materials in Nonpolar Media. V. Norbornene and Nortricyclene[1]

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Chlorination of norbornene in carbon tetrachloride solution at 25° in the presence of oxygen to inhibit radical reactions and isolate the ionic pathway gave nortricyclyl chloride (I), exo-2-syn-7-dichloronorbornane (II), trans-2,3- (V), and exo-cis-2,3-dichloronorbornane (III) in a ratio of 65:25.5:6:3.5. In the absence of inhibitors and added initiators, dark chlorination led to spontaneous radical reaction (superimposed on the ionic reaction), the fraction of which increased with increasing norbornene concentration. From several runs under dark and illuminated conditions, the purely radical product distribution has been calculated as: I (18%), III (34%), V (38%), exo-5-chloronorbornene (VI, 7%), and endo-5-chloronorbornene (VII, 3%). The ratio of I:VI from photochlorination of norbornene with t-butyl hypochlorite increases with decreasing hypochlorite concentration. The nature of the intermediates in these ionic and radical chlorinations is considered. Treatment of norbornene with iodobenzene dichloride gave III in moderate yield along with V. Photochlorination of nortricyclene gave approximately equal amounts of a monochloride fraction, which was largely I but also contained VI, and a dichloride fraction, which was largely exo,exo-2,6-dichloronorbornane (XIX). This latter product is formulated as the result of chlorine atom attack on a cyclopropyl carbon atom with inversion.

Introduction

Chlorination of norbornene in pentane solution at −78° has been reported[2] to give 43% nortricyclyl chloride (I) and 37% *exo*-2-*syn*-7-dichloronorbornane (II); ionic intermediates were postulated to explain these results. Olefin chlorinations in nonpolar solvents have recently been shown[3] to involve a duality of mechanism; whereas chlorination of several branched olefins does indeed involve solely ionic intermediates, chlorination of several linear and cyclic olefins proceeds largely through free-radical intermediates because of initiation of radical-chain reactions by interaction of the olefin and chlorine; as an added complication, the percentage of radical reaction for a given olefin decreases as the concentration of olefin decreases. In light of these results and in light of current interest in addition reactions of norbornene and its analogs,[4–6] it appeared interesting to reinvestigate the chlorination of norbornene with the help of more recent analytical techniques.

Results

Treatment of norbornene in carbon tetrachloride solution at 25° with a limited amount of chlorine (<10 mole %) in the presence of oxygen (to inhibit radical reactions) gave a reaction mixture which showed four peaks in the g.l.p.c. spectrum on a poly(propylene glycol) column in a ratio of 65:6:3.5:25.5[7] (in order of increasing retention time). Isolation of the first and last showed them to be I and II, respectively, identical with the products isolated by Roberts and

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[1] (a) Presented in part before the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; for part IV, see M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4285 (1965); (b) norbornene = bicyclo[2.2.1]heptene; nortricyclene = tricyclo[2.2.1.$0^{2,6}$]heptane.

[2] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

[3] M. L. Poutsma, *ibid.*, **87**, 2161, 2172 (1965).

[4] For representative ionic addition reactions see (a) bromine: J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950), and H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); (b) peracids: H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954); (c) aromatic sulfenyl halides: H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956); S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *ibid.*, **79**, 6035 (1957); H. Kwart, R. K. Miller, and J. L. Nyce, *ibid.*, **80**, 887 (1958); (d) alcohols: S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962); (e) mercuric salts: T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963); (f) hydrogen bromide: H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).

[5] For representative radical addition reactions, see (a) bromine: J. A. Berson and R. Swidler, *ibid.*, **76**, 4060 (1954); (b) thiophenols: S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954); S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957); (c) aromatic sulfonyl halides: S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961); (d) ethyl bromoacetate: J. Weinstock, Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 1955, p. 19-O; (e) polyhalomethanes: E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964); (f) perfluoroalkyl iodides: N. O. Brace, *ibid.*, **27**, 3027 (1962); (g) acetone: W. Reusch, *ibid.*, **27**, 1882 (1962); (h) hydrogen bromide: ref. 4f, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 623 (1960); (i) *t*-butyl hypochlorite: E. Tobler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, **29**, 2834 (1964); (j) formamide: D. Elad and J. Rokach, *J. Chem. Soc.*, 800 (1965).

[6] For miscellaneous addition reactions see (a) phthaloyl peroxide: F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **82**, 890 (1960); (b) nitrosyl halides: J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **86**, 4074 (1964); (c) benzophenones photochemically: D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (d) 1,3-dipolar additions: R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); (e) benzenesulfonyl azide: J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964).

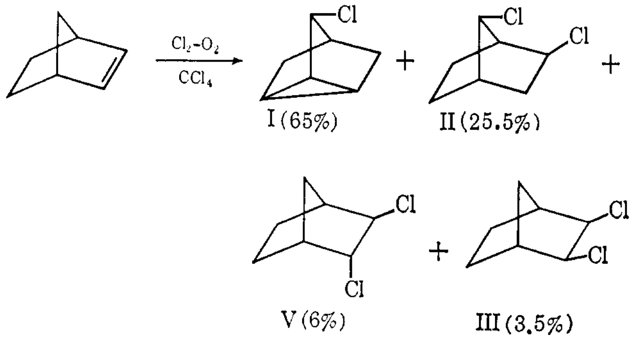
[7] All g.l.p.c. areas have been converted to molar quantities by use of appropriate calibration factors determined from mixtures of known compounds.

Table I. Dependence of Product Composition on Reaction Conditions for Chlorination of Norbornene at 25°

Entry	Mole fraction of norbornene[a]	Conditions	I[b]	II[b]	III[b]	V[b]	VI[b]	VII[b]
1	0.52	Oxygen; dark	63.3	26.6	4.5	5.5	*c*	*c*
2	0.22		65.4	25.7	3.4	5.5	*c*	*c*
3	0.043		65.5	25.1	3.3	6.1	*c*	*c*
4	0.022		65.4	25.5	3.0	6.1	*c*	*c*
5	0.65	Nitrogen; dark	45.0	19.6	9.8	20.5	3.5	1.6
6	0.49		50.1	21.6	8.1	16.2	2.8	1.2[d]
7	0.46		57.0	18.7	6.0	14.6	2.7	1.1
8	0.32		54.8	21.6	7.1	13.2	2.3	0.9[d]
9	0.22		56.9	24.2	4.9	11.7	1.7	0.7
10	0.16		57.9	24.0	6.0	10.4	1.2	0.6
11	0.099		58.8	23.3	4.9	11.5	1.1	0.4
12	0.069		60.3	25.6	4.6	8.4	0.7	0.3
13	0.049		61.5	25.7	3.7	8.2	0.6	0.25[d]
14	0.032		59.7	25.6	4.9	8.9	0.6	0.25[d]
15	0.025		62.3	25.5	3.6	8.1	0.5	0.2
16	0.013		61.6	25.6	4.3	8.1	0.2	0.1[d]
17	0.22	Nitrogen; light[e]	47.7	17.8	10.5	18.8	3.6	1.5[d]
18	0.077	Nitrogen; light[f]	28.8	5.6	28.5	30.1	5.0	2.1[d]
19	0.055	Nitrogen; light[f]	40.5	12.7	18.5	22.5	4.1	1.7[d]
20		*g*	64.9	25.7	3.6	5.8	0	0
21		*h*	18.8	0	35.4	36.8	6.4	2.7
22		*i*	16.6	0	33.1	38.8	8.1	3.4

[a] In carbon tetrachloride. [b] Percentage of total observed products. [c] Not detected by g.l.p.c.; <0.1%. [d] Derived from VI and average VII:VI ratio; see text. [e] Three 275-w. sunlamps at *ca.* 6 in. through Pyrex. [f] High-pressure mercury arc through quartz; see Experimental Section. [g] Average ionic product distribution; average of entries 1–4. [h] Radical product distribution based on entry 18 corrected for partial ionic reaction; see text. [i] Radical product distribution based on entry 19.

co-workers.[2] The second peak had a retention time on several columns equal to that of *trans*-2,3-dichloronorbornane (V) and the third to that of *exo-cis*-2,3-dichloronorbornane (III). Neither of these minor products was isolated in pure form from a chlorination run under oxygen but distillation fractions boiling between the major products, I and II, had infrared spectra consistent with the present assignment. Since, in known mixtures, dichloride II was only partially resolved from *endo-cis*-2,3-dichloronorbornane (IV), only an upper limit (<5% of the amount of II) can be set for the amount of IV in the chlorination product although no positive evidence for its presence was ever obtained. The product distribution was rather insensitive to norbornene concentration as shown in entries 1–4 of Table I. As expected from the observed formation of I, hydrogen chloride was evolved in these chlorinations. However, control experiments showed that treatment of norbornene with dry hydrogen chloride at 25° in carbon tetrachloride solution gave negligible reaction during the time of a typical chlorination run (*ca.* 5 min.); this conclusion was supported by the failure to detect (g.l.p.c.) *exo*- (IX) or *endo*-2-chloronorbornane (X) in the chlorination product. Also, hydrogen chloride was shown not to react with I under the reaction conditions. The product composition was insensitive to the degree of conversion (1–10%) or to the length of time elapsed after reaction before g.l.p.c. analysis. Finally, the behavior of authentic samples of the reaction products gave no evidence for rearrangements on the g.l.p.c. column. Therefore, the observed products represent the kinetically controlled product distribution.



Dark chlorination of a dilute solution of norbornene in carbon tetrachloride (mole fraction = 0.01–0.02) under nitrogen gave a product distribution only slightly different from that of a corresponding reaction under oxygen (*cf.* entries 15 and 16 of Table I with entry 4). However, as the concentration of olefin was progressively increased in a series of otherwise identical dark runs under nitrogen (entries 5–16 of Table I), a trend toward increased III and V and decreased I and II became apparent until, at mole fraction 0.65, the 2,3-dichlorides made up 30% of the total product compared to 10% at a comparable concentration under oxygen. This trend is illustrated in Figure 1; the lines are drawn straight to show the general behavior and no further significance is implied. At the same time, two new peaks, of retention time close to those of the other monochlorides encountered in this study, appeared and became progressively more intense until, at mole fraction 0.65, they made up *ca.* 5% of the product. The compounds responsible have not been isolated in pure form, but they had retention times on several columns identical with those of *exo*- (VI) and *endo*-5-chloronorbornene (VII) and different from those of *syn*- (XI) and *anti*-7-chloronorbornene (XII) and 2-chloronorbornene (VIII). Neither VIII nor XII, both of which had retention times distinct from those of any of the other monochlorides considered, could be detected (the limit is <5% of VI). The retention time of XI was the same as that of I on the column employed; however, its absence could be concluded from infrared evidence (*vide infra*). Since definite infrared evidence for the presence of VI was obtained, we assign the minor products as VI and VII. The area of the peak assigned to VII was difficult to measure accurately in all runs because it occurred close to that for I; an average value of VII:VI (0.42) was determined from seven random runs (in which the peak for VII was the most distinct) for which VII:VI varied between extreme values of 0.39 and 0.45; the values for VII in Table I are thus measured values if unmarked but are calculated from 0.42 (VI) where so noted. If carbon tetrachloride was replaced by cyclohexane as solvent, chlorocyclohexane was produced in dark runs under nitrogen but not under oxygen.

Repetition of chlorination under nitrogen with illumination from three 275-w. sunlamps at *ca.* 6 in. enhanced the trend toward increased III and V at the expense of I and II at a given olefin concentration (*cf.* entries 9 and 17 of Table I). When illumination was provided by an intense ultraviolet source (entry 18), the 2,3-dichlorides could be forced to make up as much as 58% of the total product; in this particular run, II decreased to 22% of its value under oxygen whereas I decreased to 44% of its corresponding value under ionic conditions. A preparative run was carried out, with the use of the ultraviolet source, from which three major sets of fractions were obtained by distillation. Infrared analysis showed the lowest boiling fractions to be mainly I; however, all the strong bands of VI (especially those at 1280, 940, and 725 cm.$^{-1}$ where I has negligible absorption) were evident and the spectrum was not inconsistent with the presence of a small amount of VII; there was no evidence for even trace absorption at 830 and 710 cm.$^{-1}$, the strongest bands in XI. An intermediate fraction was shown to be largely the *trans* dichloride V by infrared analysis. Finally, the highest boiling materials had infrared spectra consistent with their being mixtures of dichlorides II and III.

Recently the photoinitiated reaction of norbornene with *t*-butyl hypochlorite has been reported[5i] to give 20–25% of a mixture of monochlorides I and VI along with the predominant radical addition products. Brief examination of this reaction, by use of the g.l.p.c. analytical techniques worked out for the chlorination reaction, has shown that I and VI are indeed the major substitution products and that their ratio is dependent on the concentration of *t*-butyl hypochlorite as shown in Table II. A minor peak was observed with the correct retention time for VII although it was not positively identified; in any case, the ratio of VII:VI must be <0.07 compared to 0.42 from the radical chlorination runs.

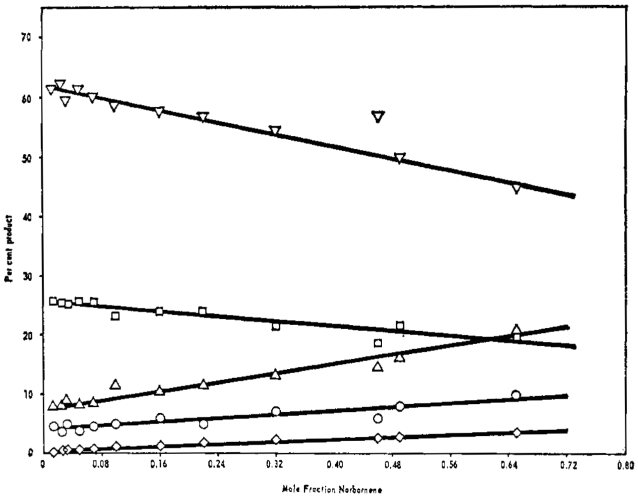


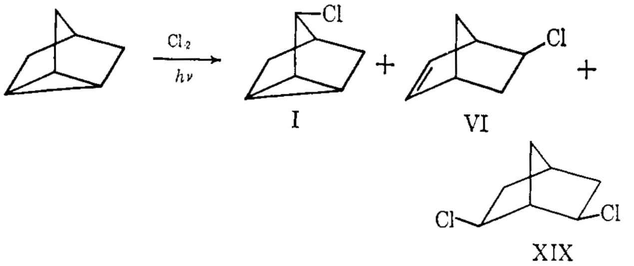
Figure 1. Dependence of product yields from chlorination of norbornene at 25° on concentration in carbon tetrachloride: ▽, nortricyclyl chloride (I); □, *exo*-2-*syn*-7-dichloronorbornane (II); △, *trans*-2,3-dichloronorbornane (V); ○, *exo*-*cis*-2,3-dichloronorbornane (III); and ◇, *exo*-5-chloronorbornene (VI).

Table II. Dependence of Ratio of Monochlorides on *t*-Butyl Hypochlorite Concentration from Reaction with Norbornene[a]

Molarity of hypochlorite	I:VI
0.44	0.31
0.22	0.38
0.088	0.59
0.044	0.79
b	1.81

[a] 2.29 *M* solution of norbornene in carbon tetrachloride treated with appropriate amount of hypochlorite under nitrogen at 25° with illumination; reaction time *ca.* 10 min. [b] Same amount of hypochlorite as in first entry added dropwise in carbon tetrachloride solution over a 30-min. period with constant illumination.

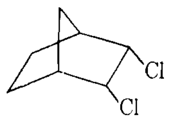
Passage of chlorine into a 0.23 *M* solution of nortricyclene in 1,1,2-trichlorotrifluoroethane with illumination to 15% conversion gave a product mixture the g.l.p.c. spectrum of which showed approximately equal amounts of mono- and dichloride products based on retention times. The monochloride region showed chiefly two bands with retention times on several columns identical with those of nortricyclyl chloride (I) and *exo*-5-chloronorbornene (VI) in a ratio of VI:I = 0.20; two trace peaks were observed, one of which had the correct retention time for *endo* isomer VII. The dichloride region showed a major band which accounted for 80–85% of the total area of the region along with two minor bands. In a second experiment, identical except that illumination was provided only after all the chlorine had been added (no apparent dark reaction), the product distribution was essentially identical except that VI:I = 0.09. From a larger scale run, the major substitution product was isolated and shown to be I by infrared spectroscopy. The major dichloride was also isolated in ~90% purity and gave an elemental analysis consistent with a dichloronorbornane. The n.m.r. spectrum showed a triplet (*J* ~ 6 c.p.s.) at 3.75 p.p.m. with each line showing barely resolvable fine structure, an unresolved line (width at half-height = 4 c.p.s.) at 2.63, a much broader unresolved line (width at half-height = 8–9 c.p.s.) at 2.43, and complex absorption between 2.2 and 1.5



I VI XIX

p.p.m. with the relative areas 2.0:0.95:0.95:6.1; there was trace absorption at 4.53 p.p.m. The following conclusions are suggested by the spectrum. (1) The single band system for two protons (3.75 p.p.m.) in the region expected for protons α to chlorine suggests that the chlorines are in identical positions; since the properties of the compound were different from those of the three 2,3-isomers, the chlorines must be at positions 2 and 5 or 2 and 6 and both *exo* or both *endo*. (2) The position (3.75 p.p.m.) of this band suggests that the chlorines are *exo* since *endo* protons have generally been observed at higher field (3.78 p.p.m. in *exo*-2-chloronorbornane (IX) and 4.03 p.p.m. in *exo-cis*-2,3-dichloronorbornane (III)) than *exo* hydrogens in corresponding compounds (4.15 p.p.m. in *endo*-2-chloronorbornane (X) and 4.32 p.p.m. in *endo-cis*-2,3-dichloronorbornane (IV)). In fact, the trace absorption observed at 4.53 p.p.m. is probably a result of a small amount of contamination by an *exo–endo* isomer. (3) The presence of two distinct bands in the region expected for bridgehead protons (2.63 and 2.43 p.p.m.), one relatively narrow and the other broad, is consistent if one of these protons has *no* adjacent *exo* hydrogens and the other one does (the major coupling of the bridgehead protons in the norbornane system is to the adjacent *exo* protons[8]); hence only the *exo,exo* 2,6 structure is possible. (4) The multiplicity of the 3.75-p.p.m. band corresponds very closely to that observed for the proton α to chlorine in IX which shows a triplet ($J \sim 5$ c.p.s.) with further fine structure at 3.78 p.p.m., but is quite different from that of X which shows at least five complex lines centered at 4.15 p.p.m., each separated by $\sim$5 c.p.s. The cumulative n.m.r. evidence is thus uniquely consistent with the structure *exo,exo*-2,6-dichloronorbornane (XIX).

For determination of g.l.p.c. retention times and area calibration factors,[7] authentic samples of compounds IV–XII were prepared by literature methods. The *exo-cis*-dichloride III has not been reported. Treatment of norbornene in carbon tetrachloride solution with iodobenzene dichloride[9] gave a mixture of primarily two products, the lower boiling of which was shown to be V; the less volatile we assign as III. Elemental analysis was consistent with a dichloronorbornane. Treatment with potassium *t*-butoxide in dimethyl sulfoxide solution gave 2-chloronorbornene (VIII) identical with that obtained from similar dehydrochlorination of *trans* dichloride V; thus a 2,3-dichloronorbornane is indicated. Since the infrared spectrum of the new compound is similar to, but distinct from, that of IV or V, structure III is the only remaining possibility. The n.m.r. spectrum of III shows a clean doublet (J = *ca.* 2 c.p.s.) at 4.03 p.p.m. as expected for the *endo* protons adjacent to chlorine split by the *anti*-7-proton.[6b,8] For comparison, the n.m.r. spectrum of the *endo-cis*-dichloride IV shows a triplet at lower field (4.32 p.p.m.) with *ca.* 4 c.p.s. between the outer lines for the *exo* protons split by the bridgehead protons; *trans*-dichloride V shows a triplet at 3.67 p.p.m. (*endo*-H) and a multiplet at 4.23 p.p.m. (*exo*-H). These features of the latter two spectra are in complete accord with those reported[8] for the corresponding *endo-cis*-5,6-dichloro- and *trans*-5,6-dichloronorbornenes.



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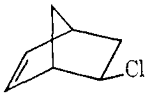

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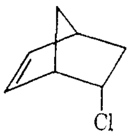

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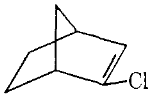

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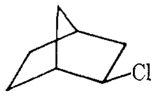

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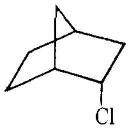

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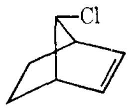

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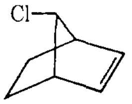

XII

Discussion

Ionic Pathway. Chlorination of norbornene in carbon tetrachloride solution under oxygen is an ionic reaction with a product distribution shown in entry 20 of Table I (average of entries 1–4); the absence of attack on concurrently present cyclohexane (as well as the absence of products VI and VII) demonstrates the absence of radical reactions. Such polar additions to norbornene have been demonstrated[4] to produce three classes of products depending on the nature of the addend and the medium: (1) *cis* addition without skeletal rearrangement, (2) *trans* addition without rearrangement, and (3) rearrangement to *exo*-2-*syn*-7 products generally accompanied by nortricyclyl products. For example, oxymercuration[4e] and addition of nitrosyl chloride[6b] (if polar) lead to *exo-cis* products, addition of aromatic sulfenyl halides[4c] leads predominantly to *trans* products, peroxidation[4b] leads mainly to rearranged diols, and bromination[4a] gives mixtures of *trans* and rearranged products. The present results seem to be the first case in which all three types of addition products have been observed in a single reaction although application of g.l.p.c. might well reveal a similar situation with several other additions. The balance among these reaction modes has been explained[4e,10] by postulating two general types of ions: (1) an ion such as XIII with the adding electrophile bridged between C-2 and C-3 which should lead to *trans* addition by backside nucleophilic attack (or apparently *cis* addition if the bridging atom carries nucleophilic ligands with it as in oxymercuration) and (2) a nonclassical ion such as XIV with carbon bridging (or the alternative rapidly equibrating pair of classical ions) which should lead predominantly to *exo*-2-*syn*-7 product by nucleophilic attack at C-1 or *cis* product by attack at the more sterically shielded C-2. This latter ion also appears to be the predominant precursor of nortricyclyl products by proton loss from C-6. Good bridging atoms such as sulfur

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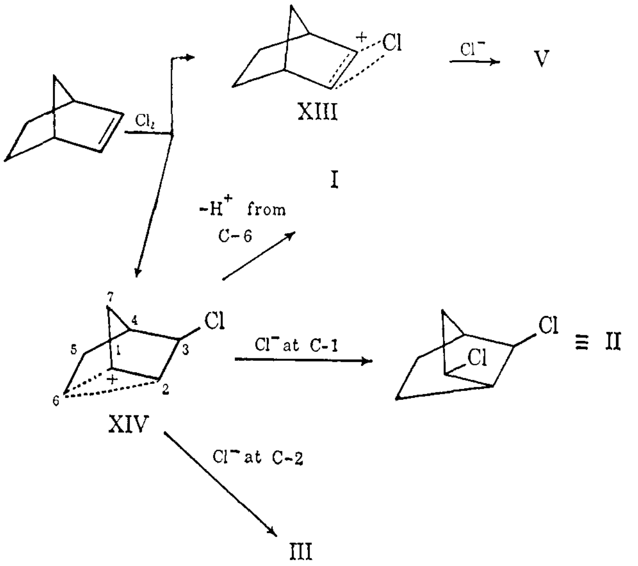
[8] P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

[9] This reagent in nonpolar solvents generally gives behavior different from that of free chlorine; however, the five-center mechanism proposed to explain a *cis* addition, [D. H. R. Barton and E. Miller, *ibid.*, 72, 370 (1950)] is not in accord with more recently reported *trans* additions: S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *ibid.*, **78**, 4939 (1956), and R. K. Summerbell and H. E. Lunk, *ibid.*, **79**, 4802 (1957). Our preliminary examination of this reagent appears to support a radical mechanism: *cf.* G. Bloomfield, *J. Chem. Soc.*, 114 (1944). Recently, radical chlorination of saturated hydrocarbons by iodobenzene dichloride has been demonstrated: D. F. Banks, E. S. Huyser, and J. Kleinberg, *J. Org. Chem.*, **29**, 3692 (1964).

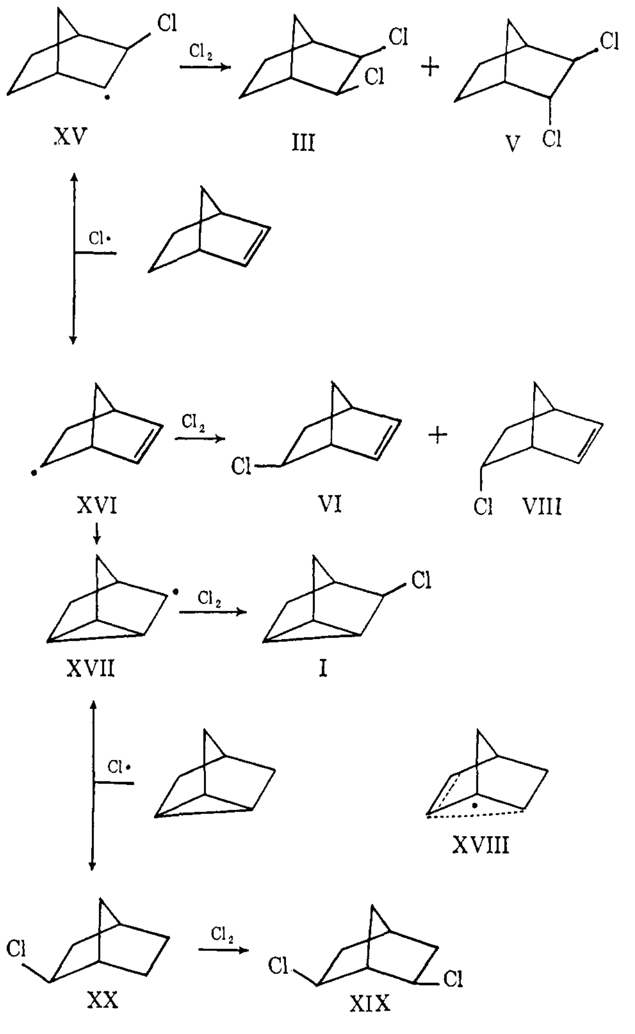
[10] L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

or mercury which form relatively weak single bonds to carbon appear to favor ions of type XIII while poor bridging atoms such as oxygen which form strong bonds to carbon favor ions of type XIV.[4e,10] The major portion of the products from chlorination of norbornene (I, II, and possibly III) is obviously derived from an ion such as XIV. Hence the present results support the previous correlations[4e,10] which had assigned chlorine as a relatively poor bridging addend on the basis of predominant (and possibly exclusive) production of I and II[2]; however, the previously undetected presence of a minor amount of *trans* addition suggests that some bridging occurs and that both types of ions are needed to explain the total chlorination products.



Radical Pathway. Dark chlorination of norbornene in the absence of oxygen and added initiators leads to attack on cyclohexane and hence to a certain fraction of radical reaction[3]; the changes in composition of the norbornene-derived products are also reasonably explained by this postulate. Consider first the illuminated runs (entries 17–19 of Table I) in which the percentage of radical reaction (r) should be the highest of the several reactions studied. If we assume that radical reaction does not lead to 2,7-disubstituted products,[5] then we can use the amount of product II as a measure of residual ionic reaction. If the corresponding amounts of products I, III, and V derived from ionic reaction (based on the distribution shown in entry 20) are subtracted from the observed amounts, a radical product distribution can be calculated as shown in entries 21 and 22 (normalized to 100%). Entry 21 is based on run 18 for which $r = 78$ and entry 22 is based on run 19 for which $r = 51$. The radical chlorination thus appears to produce I, III, V, VI, and VII in a ratio of 18:34:38:7:3. Note particularly that the nortricyclyl derivative I has not gone to zero and hence is a true radical product.

Attack of chlorine atom on norbornene would be expected to result in both addition to the double bond and hydrogen abstraction in the same fashion as observed for other olefins.[3] Addition of several radicals to norbornene and its analogs has been studied[5] with both *cis*[5a,b,d] and *trans*[5c,e,f,i] addition having been observed. A recent study[4f] of radical addition of deuterium bromide to norbornene has revealed not only mixtures of *cis* and *trans* addition but also 20% of bromine atom attack from the *endo* side in contrast to the prevailing assumption[5] that initial attack occurs only from the more accessible *exo* side. The present results show that radical chlorine addition gives comparable amounts of *cis* and *trans* addition. However, the exact nature of the intermediate radical (or radicals) XV (*exo*-chlorine, *endo*-chlorine, or bridged) cannot be specified with only this information. The abstraction products I, VI, and VII can all be derived by abstraction of hydrogen from the two-carbon bridge to give radical XVI. This view is reasonable since photochlorination of norbornane leads to predominant formation of 2-chloro products with only traces of 7- and no 1-chloro products[11]; hence attack on the two-carbon bridge is greatly favored over attack at the one-carbon bridge or at the bridgehead. Radical XVI apparently not only reacts directly with chlorine to produce VI and VII with an *exo*:*endo* ratio of *ca.* 2.4 (*exo*:*endo* is *ca.* 3 for the 2-norbornyl radical)[11a] but also cyclizes to the nortricyclyl radical XVII. Wilt and Levin[12a] observed that the hydrocarbon fraction from decarbonylation of norborn-2-ene-*endo*-5-



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(11) (a) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); (b) C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

(12) (a) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962); (b) D. J. Trecker and J. P. Henry, *J. Am. Chem. Soc.*, **85**, 3204 (1963), and references therein; see also E. S. Huyser and G. Echegaray, *J. Org. Chem.*, **27**, 429 (1962).

carboxaldehyde contained both norbornene and nortricyclene. Also, cyclization of 5-substituted norborn-2-en-6-yl radicals to nortricyclyl radicals has been observed as the predominant reaction course in most radical additions to norbornadiene.[12b] If our proposed pathway is correct, the ratio of I:(VI + VII) should increase as the concentration of chlorine decreases. If, however, the intermediate leading to I and VI is solely a nonclassical species (XVIII), the product ratio should be insensitive to the concentration of the chain-transfer agent.[13] Because of the difficulties of attaining a significant fraction of radical reaction and of controlling the chlorine concentration, this criterion could not be applied to the norbornene–chlorine reaction. However, the *t*-butyl hypochlorite reaction[5i] should involve the same norbornene-derived intermediates (XVI and XVII or XVIII) leading to products I, VI, and VII. Here the starting concentration of chain-transfer agent can be controlled and, as shown in Table II, the ratio of I:VI does increase with decreasing hypochlorite concentration as predicted for classical radicals XVI and XVII; obviously XVIII could not be the sole intermediate.

Photochlorination of nortricyclene was examined since this reaction should generate nortricyclyl radical XVII directly by hydrogen abstraction. The observation that the resulting monochlorides included some VI (and apparently VII) as well as I shows that, not only can cyclization of radical XVI to radical XVII occur rapidly enough to compete with chain transfer with chlorine (*vide supra*), but also the reverse ring opening is a rapid reaction. In the two runs conducted, the ratio of VI:I behaved as predicted; *i.e.*, lower average chlorine concentration led to relatively more VI. However, this result is not rigorous since some of the unsaturated product VI could have been consumed by ionic reaction with chlorine. The major dichloride product XIX can be formulated as the result of ring opening of a cyclopropane ring by chlorine atom; such a process has been observed previously for cyclopropane[14] and spiropentane.[15] The observed *exo,exo* stereochemistry suggests attack on carbon with inversion followed by predominant chain transfer of radical XX from the *exo* side.[11a] Because of the special steric constraints in nortricyclene, one cannot safely generalize that inversion will be the preferred pathway for cyclopropane itself, but at least it is obvious that rear-side displacement by chlorine atom on cyclopropyl carbon is a facile process. Inversion has recently been observed in a radical ring opening of a highly strained cyclobutane by bromine atom.[16]

A crude estimate can be made of the relative reactivity of the norbornene double bond compared to other olefins toward chlorine atom. The 2-hydrogens of norbornane have been shown to have a relative reactivity very similar to that of cyclohexyl hydrogens[11b] (where we define $k_t = 1.00$ for abstraction of a single hydrogen from cyclohexane[3]). If the same reactivity holds for the four hydrogens of norbornene on the two-carbon bridge, the observed radical addition–abstraction ratio ((III + V):(I + VI + VII)) of 2.6 (entries 21 and 22 of Table I) can be translated into $k_a = 10.4$ where k_a is the relative rate of chlorine atom addition to norbornene as a whole. This value is close to the values determined[3] for 1- and 2-butene ($k_a = 10$–12). Since several assumptions have preceded this value for k_a, it is surely approximate at best; however, it does support the over-all consistency of the proposed reaction scheme.[17]

Ionic–Radical Competition. Finally, we can consider the position of norbornene in the family of olefins as far as chlorination behavior is concerned. Previously we have shown that chlorination of olefins in the absence of inhibitors and external initiators involves a competition between ionic reactions and spontaneous radical initiation which leads to radical reactions. Chlorination of neat mono- and 1,2-disubstituted olefins such as cyclohexene[3] or the linear butenes[3] (or of concentrated solutions in nonpolar solvents) led predominantly to radical reaction; ionic reactions became important only at low concentrations (mole fractions <0.1). On the other hand, chlorination of branched olefins such as isobutylene[1,3] led essentially completely to ionic reaction at all concentrations. Norbornene falls between these extremes; at low concentration, chlorination is predominantly ionic; as the concentration is increased, radical reactions become significant but never exceed *ca.* 25% even at the highest concentrations attainable in nonpolar solvents.

Experimental Section

Infrared spectra were determined as 10% solutions in carbon disulfide on a Beckman IR5A instrument; n.m.r. spectra were determined as 20% solutions in carbon tetrachloride on a Varian A-60 instrument and results are expressed in p.p.m. downfield from internal TMS; boiling points are uncorrected.

Materials. Norbornene (Columbia Organic Chemicals) was sublimed under vacuum before use. Isomerization of norbornene[18] gave a mixture rich in nortricyclene from which the latter was isolated by preparative g.l.p.c.; such material was >99.9% pure with no norbornene detectable by g.l.p.c. analysis. Carbon tetrachloride was purified by the method described by Fieser.[19]

Quantitative Chlorination Procedure. The procedure was identical with that described[3] previously except that the amounts of norbornene used were determined by weight; in a typical run (Table I) the mixture of norbornene and carbon tetrachloride (10–15 ml.) was treated with 0.3–1.0 mmole of chlorine. The g.l.p.c. analysis is described below The ultraviolet-initiated runs (entries 18 and 19 of Table I) were carried out by use of a 450-w. Hanovia high-pressure mercury lamp placed in a water-cooled quartz immersion well centered in a 150-ml., cylindrical, water-cooled reactor; the chlorine–nitrogen mixture was introduced directly adjacent to the most intense section of the lamp.

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[13] There seems to be no compelling evidence for such a species when generated by radical addition to an appropriate diene[12b] or by perester decomposition: M. M. Martin and D. C. DeJongh, *J. Am. Chem. Soc.*, **84**, 3526 (1962).

[14] C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962).

[15] D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *ibid.*, **82**, 2368 (1960).

[16] D. E. Applequist and R. Searle, *ibid.*, **86**, 1389 (1964).

[17] For example, toward addition of the trichloromethyl radical, norbornene is some 1.2 times as reactive as 1-octene: M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[18] P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

[19] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1957, p. 283.

G.l.p.c. Analyses. All analyses described in Table I were performed on a Micro-Tek 2500R instrument equipped with 2-m. Perkin-Elmer "R" columns (poly-(propylene glycol)) operated at 105° for 20 min. and then programmed to 145° in 5 min. At a helium flow of *ca.* 200 ml./min., the retention times in minutes were: VIII, 9; XII, 10.5; VI, 11; VII, 13; IX and X, 13.5; I and XI, 15; V, 29.5; XIX, 35; III, 43; IV, 46.5; and II, 47. A flame ionization detector was used and areas (determined from the product of peak height and retention time) were corrected to molar quantities by means of calibration factors obtained from identical analysis of standard mixtures. Analyses were also performed on Perkin-Elmer columns "A" (diisodecyl phthalate), "O" (silicone grease), and "Q" (Apiezon grease); on each, the retention times of III, V, VI, and VII were identical with those of the chlorination products to which these structures have been assigned.

Preparative Chlorination of Norbornene under Ionic Conditions. A solution of 77.7 g. (0.83 mole) of norbornene in 150 ml. of carbon tetrachloride was cooled to 0°. Chlorine (23 ml. of liquid, *ca.* 0.5 mole) was then swept into this solution with a stream of oxygen in subdued light over a 45-min. period at 0°. The reaction mixture was concentrated on a rotary evaporator at room temperature and *ca.* 20 mm. The residue was distilled directly through an 18-in. spinning-band column and the following fractions were taken: (1) 4.9 g., b.p. <61° (24 mm.); (2) 12.75 g., b.p. 61–63° (24 mm.), n^{24}D 1.4952; (3) 14.9 g., b.p. 63° (25 mm.), n^{24}D 1.4956; (4) 6.9 g., b.p. 48–50° (11 mm), n^{24}D 1.4958; (5) 5.7 g., b.p. 60–97° (9 mm.), n^{24}D 1.5055; and (6) 22.5 g., b.p. 108° (13 mm.) to 118° (20 mm.), solidified at 25°. The infrared spectra of fractions 2–4 were essentially identical with each other and with that reported[20] for nortricyclyl chloride (I) (lit.[2] b.p. 64–65° (27 mm.), n^{25}D 1.4911) (*ca.* 54% yield in fractions 2–4). G.l.p.c. analysis showed that fraction 3 was 98% pure. The infrared spectrum of fraction 6 was consistent with that reported[2] for *exo*-2-*syn*-7-dichloronorbornane (II) (lit.[2] b.p. 97–110° (11 mm.)); g.l.p.c. analysis revealed 10% of an impurity with retention time identical with that of *exo*-*cis*-2,3-dichloronorbornane (III) (*ca.* 27% yield of (II + III) in fraction 6). Redistillation gave a sample of II, b.p. 85° (3 mm.), 95.5% pure by g.l.p.c. The infrared spectrum of fraction 5 contained no bands which could not be accounted for by its being a mixture of I, II, III, and V.

Preparative Chlorination of Norbornene under Partially Radical Conditions. A solution of 25 g. of norbornene in 200 ml. of 1,1,2-trichlorotrifluoroethane was treated with 4.5 ml. (liquid) of chlorine under nitrogen with ultraviolet illumination in the reactor described above over a 15-min. period. The reaction mixture was concentrated on a rotary evaporator at room temperature and *ca.* 20 mm. The residue was distilled directly through an 18-in. spinning-band column and the following fractions taken after some residual norbornene was removed at 30 mm: (1) 0.4 g., b.p. 60–61° (32 mm.); (2) 1.8 g., b.p. 61–62° (32 mm.), n^{25}D 1.4951; (3) 0.6 g., b.p. 41–60° (9 mm.); (4) 1.8 g., b.p. 64–70° (9 mm.), n^{23}D 1.5032; (5) 1.0 g., b.p. 58–70° (3 mm.); and (6) 2.2 g., b.p. 72–76° (3 mm.), n^{23}D 1.5083. Examination of the cold trap in the vacuum line showed that significant material had been lost during this slow distillation and that the over-all yield was higher than the isolated products would indicate. The infrared spectra of fractions 1–3 showed them to be predominantly nortricyclyl chloride (I) in each case. However, fraction I showed significant bands at 1280, 940, and 725 cm.$^{-1}$, these being the strongest bands of *exo*-5-chloronorbornene (VI) which would not have been obscured by I; these bands became progressively less intense in fractions 2 and 3. In no case was there detectable absorption at 830 or 710 cm.$^{-1}$, these being the strongest bonds of *syn*-7-chloronorbornene (XI) which would not have been obscured by I. The infrared spectrum of fraction 4 showed it to be *trans*-2,3-dichloronorbornane (V). Fractions 5 and 6 gave infrared spectra, the bands of which were a composite of those of *exo*-*cis*-2,3-dichloronorbornane (III) and *exo*-2-*syn*-7-dichloronorbornane (II) with fraction 5 being richer in III than fraction 6.

Preparative Chlorination of Nortricyclene. A solution of 2.75 g. (29 mmoles) of pure nortricyclene in 10 ml. of 1,1,2-trichlorotrifluoroethane was flushed with nitrogen; liquid chlorine (1.3 ml., 30 mmoles) was allowed to vaporize and to be swept by nitrogen into the illuminated reaction mixture at 25°. The resulting mixture was partially evaporated to remove most of the solvent. G.l.p.c. examination of the residue showed the same two major products detected in smaller runs carried to low converison. The first was collected by preparative g.l.p.c. and had an infrared spectrum identical with that of nortricyclyl chloride (I). Collection of the second gave a sample which was ~80% the major dichloride (the contaminants are apparently isomeric C-7 dichlorides formed either in the initial reaction or by further reaction of I). A portion (400 mg.) was cooled to −78° and some crystals formed; the liquid was removed by centrifugation and decantation. This liquid was treated with one drop of hexane; cooling to −78° gave a second crop of crystals which were harvested in the same fasion. Successive dilutions with hexane and cooling gave five crops of solid; the combined solids were crystallized from hexane at −20°. The crystals so obtained (75 mg.) melted just below room temperature and were 90% pure by g.l.p.c. analysis. The n.m.r. spectrum and assignment as *exo*,*exo*-2,6-dichloronorbornane (XIX) have been discussed in the Results section.

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.9; H, 6.1; Cl, 43.0. Found: C, 50.8; H, 5.7; Cl, 43.3.

Preparation of Authentic Chlorinated Norbornanes. *endo*-*cis*-2,3-Dichloronorbornane (IV) was prepared by the method of Roberts, *et al.*,[2] by hydrogenation of the Diels–Alder adduct of cyclopentadiene and *cis*-1,2-dichloroethylene. A center distillation cut had b.p. 99° (8 mm.) and m.p. 50–56°; g.l.p.c. analysis showed 10% of the band assigned to III. Crystallization from hexane gave a sample, m.p. 73–77° (lit.[2] b.p. 98–105° (13–14 mm.), m.p. 74–77°), >98% pure by g.l.p.c., whose infrared spectrum was consistent with that reported.[2] The n.m.r. spectrum of IV showed a set of three lines at 4.32 p.p.m. with *ca.* 4 c.p.s. between the outer pair, which corresponded to 1.9 protons based on a total of 10 protons. *trans*-2,3-Dichloronorbornane (V) was prepared in analogous fashion from *trans*-1,2-di-

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[20] J. D. Roberts and W. Bennett, *J. Am. Chem. Soc.*, **76**, 4623 (1954).

chloroethylene; the best fraction (85% by g.l.p.c.) had b.p. 91–92° (20 mm.), n^{23}D 1.5038 (lit.[2] b.p. 85–86° (18 mm.), n^{25}D 1.5015), and an infrared spectrum consistent with that reported.[2] The n.m.r. spectrum of V had a multiplet at 4.23 and a set of three lines at 3.67 p.p.m. (*ca.* 6 c.p.s. between the outer pair) of equal area whose total area corresponded to 1.7 protons based on a total of 10 protons. *exo*-5-Chloronorbornene (VI) was prepared by addition of hydrogen chloride to norbornadiene by the method of Schmerling, *et al.*[21]; the best distillation fraction (<6% of I by g.l.p.c.) had b.p. 68° (45 mm.), n^{25}D 1.4915 (lit.[21] b.p. 66–68° (43 mm.), n^{20}D 1.4949 for a sample estimated to contain 15–20% I), and an infrared spectrum consistent with that reported.[22] *endo*-5-Chloronorbornene (VII) was prepared by Diels–Alder reaction between cyclopentadiene and vinyl chloride[10]; g.l.p.c. analysis of the distilled product showed that it was seriously contaminated with VI; a sample, $n^{23.5}$D 1.4942, was collected by preparative g.l.p.c. (94% pure) and its infrared spectrum was consistent with that reported.[22] Hydrogenation of VI in ethyl acetate solution over platinum oxide gave *exo*-2-chloronorbornane (IX), b.p. 80–81° (50 mm.), n^{24}D 1.4832 (lit.[23] b.p. 88–89° (74 mm.), n^{25}D 1.4824), whose g.l.p.c. spectrum showed 8% I (present in the starting sample of VI); the infrared spectrum was consistent with that reported.[22] A mixture of VI and VII was hydrogenated in similar fashion; the resulting distilled product showed only one major peak of retention time equal to that of IX on several columns, but the infrared spectrum had several bands in addition to those of IX. This mixture was heated in 80% ethanol for 41 hr. at 80° with solid sodium carbonate present; the organic material was recovered by flooding with water, extraction with pentane, evaporation, and distillation. A fraction, b.p. 79° (44 mm.), $n^{23.5}$D 1.4807 (lit.[21] b.p. 75° (41 mm.)), had an infrared spectrum consistent with that reported[22] for *endo*-2-chloronorbornane (X) except for a few extra bands; g.l.p.c. examination showed 10–15% of material more volatile than the major peak. No g.l.p.c. separation of IX and X was achieved on several columns.

Treatment of norbornene with acidified sodium hypochlorite solution gave a crude chlorohydrin which was converted to an ester with 2-naphthoyl chloride by the method of Roberts, *et al.*[2]; pyrolysis of the crude ester at 300° (100 mm.) as described previously[2] gave a crude product the infrared spectrum of which was consistent with that reported[2] for *syn*-7-chloronorbornene (XI). Preparative g.l.p.c. gave a sample (>98% pure by g.l.p.c.), n^{23}D 1.4975 (lit.[2] n^{25}D 1.4920). The analogous method of Roberts, *et al.*,[2] was used to prepare *anti*-7-chloronorbornene (XII) from the 2-naphthoate ester of the chlorohydrin obtained from hydrolysis of dichloride V; a sample, purified by preparative g.l.p.c., had an infrared spectrum consistent with that reported.[2]

exo-cis-2,3-Dichloronorbornane (III). Iodobenzene dichloride (*ca.* 0.5 mole) was prepared by the reported procedure[24] and partially freed from chloroform by air drying. A solution of 82 g. (0.87 mole) of norbornene in 200 ml. of carbon tetrachloride was treated with *ca.* one-fifth of the solid iodobenzene dichloride. The resulting suspension was heated to reflux with stirring. After a short induction period, a rather violent reaction commenced and the mixture quickly became homogeneous. The remainder of the solid dichloride was added in small portions over a 15-min. period at reflux. The mixture was heated at reflux an additional 15 min. Solvent and excess norbornene were removed on a rotary evaporator at *ca.* 20 mm. after which the residue was distilled through an 18-in. spinning-band column. After all material boiling below 58° (4 mm.) (presumably iodobenzene) was discarded, the following fractions were taken: (1) 33.0 g., b.p. 58–62° (4 mm.), $n^{22.5}$D 1.5108; (2) 9.5 g., b.p. 64–80.5° (4 mm.), $n^{22.5}$D 1.5172; (3) 9.5 g., b.p. 80.5 (4 mm.), $n^{22.5}$D 1.5165; and (4) 6.0 g., b.p. 81–84° (4 mm.), $n^{22.5}$D 1.5159. The infrared spectrum of fraction 1 showed it to be largely V contaminated with iodobenzene. The infrared spectrum of fraction 3 was similar to, but definitely different from, that of the *endo-cis*-2,3-, *trans*-2,3-, and *exo*-2-*syn*-7-dichlorides; the n.m.r. spectrum showed a doublet (J = *ca.* 2 c.p.s.) at 4.03 p.p.m. corresponding to 1.8 protons based on a total of 10 protons. G.l.p.c. analysis of fraction 3 revealed 10% of a compound with a retention time similar to that of II or IV. An analytical sample was prepared by redistillation of fraction 3.

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.9; H, 6.1; Cl, 43.0. Found: C, 50.9; H, 6.0; Cl, 43.0.

Treatment of fraction 4 with excess potassium *t*-butoxide in dimethyl sulfoxide solution for 12 hr. at 75° followed by dilution with water, extraction with pentane, and distillation gave 2.0 g. (43%) of 2-chloronorbornene (VIII), b.p. *ca.* 45° (20 mm.), $n^{22.5}$D 1.4863. The infrared spectrum of this sample was essentially identical with that of a larger sample of VIII, prepared in analogous fashion from the *trans*-dichloride V, b.p. 40–41° (17 mm.), n^{24}D 1.4886 (lit.[2] b.p. 50–54° (41 mm.), n^{25}D 1.4875), and >98% pure by g.l.p.c. analysis.

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(21) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).

(22) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

(23) J. D. Roberts, L. Urbanek, and R. Armstrong, *ibid.*, **71**, 3049 (1949).

(24) H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 482.