

## BICYCLANES—I

### THE HALOGENATION OF 2:2:1-BICYCLOHEPTANE (NORBORNANE\*)

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**Abstract**—The free-radical halogenation of norbornane gives mainly the 2-halides; *exo/endo* ratios depending on the nature of the halogen donor. Molecular chlorine or bromine give about 70 per cent of *exo*- and 20–25 per cent of *endo*-halides:  $\text{SO}_2\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{PCl}_5$  and  $\text{CBrCl}_3$  give 95 per cent of the *exo*-isomer. This increased stereospecificity is ascribed to the relatively lower accessibility of the intermediate 2-norbornyl radicals from the *endo*-side for the bulkier reagents.

A small proportion of the 7-chloride was observed in the chlorinations with  $\text{Cl}_2$ ,  $\text{SO}_2\text{Cl}_2$  and  $\text{PCl}_5$ ; the bridgehead chloride (1) could not be detected.

Competitive halogenations of norbornane and *cyclohexane* indicate that the methylene groups in *cyclohexane* and in the six-membered ring of norbornane are about equally reactive towards various attacking radicals.

STRAINED bicyclic compounds often display peculiar rearrangements and stereospecific reactions, which are less common with related monocyclic or strainless compounds, and it seemed of interest to investigate the behaviour of some simple bicyclanes in relation to their molecular structures.

The present paper is the first of a planned series in which the emphasis will be on “nor-compounds” rather than on their polymethylated homologues such as those occurring in many natural products, the main object being to compare the chemical behaviour of the strained bicyclic skeleton with that of related strainless systems.

2:2:1-Bicycloheptane (norbornane\*) was first prepared by Komppa and Beckmann who designated it as “norbornylene”. The molecule may be depicted as the boat form of *cyclohexane*, a methylene bridge being attached to the 1 and 4 positions (A); for the purpose of illustrating chemical reactions the arrangement B is more usual:

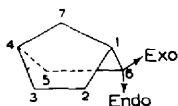


FIG. A

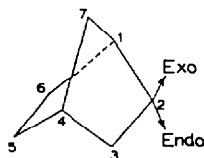


FIG. B

The geometry of the molecule is such that an appreciable strain should occur. Alder and Stein,<sup>2</sup> by comparison of heats of combustion of norbornane derivatives and their strainless isomers, have estimated that the strain energy should amount to

\* The names norbornane and norcamphane for bicycloheptane are both used in recent papers and textbooks. Norbornane is the name accepted by the Commission on Nomenclature of the I.U.P.A.C.

<sup>1</sup> G. Komppa and S. Beckmann, *Ann.* **512**, 172 (1934).

<sup>2</sup> K. Alder and G. Stein, *Ber. Dtsch. Chem. Ges.* **67**, 613 (1934); cf. G. Becker and W. A. Roth, *Ibid.* 627. For pioneering work of Alder *et al.* see *Ann.* **504**, 228 (1933); **513**, 1, 197, 211 (1934); **525**, 183, 221 247 (1937).

about 6 kcal. Considerations of models suggest that the (3,4,5) angle and the (1,7,4) angle should be appreciably smaller than the tetrahedral value. This assumption is supported by recent findings in this laboratory.<sup>3</sup>

The close proximity of 2- and 6-positions in norbornane (about 2.2 Å)<sup>3</sup> may be related to the participation of 6-positions in solvolytic reactions involving 2-derivatives. In *cyclohexane*, the distance between 1- and 3-positions is normal (about 2.5 Å); these effects do not occur here.<sup>4,5</sup>

From a standpoint of chemical reactivity norbornane has received but little attention. Gas phase nitration has been reported to give the 1-isomer in low yields.<sup>6</sup> Free-radical initiated chlorination has been briefly studied by Roberts *et al.* and by West and Schmerling,<sup>8</sup> using sulphuryl chloride and carbon tetrachloride respectively, and according to the former authors the product was 95 per cent *exo*-2-chloride, whereas West and Schmerling concluded that the monochlorides consisted of about 90 per cent of 2-norbornyl-chloride.

The present paper deals with free-radical initiated mono halogenations of norbornane by means of various reagents, viz. with Cl<sub>2</sub>, CCl<sub>4</sub>, SO<sub>2</sub>Cl<sub>2</sub> and PCl<sub>5</sub> (chlorinations) and with Br<sub>2</sub>, CBrCl<sub>3</sub> and N-bromosuccinimide (brominations). The mechanism involved in reactions of this type may be represented by the following scheme:



This scheme is known to hold with the molecular halogens (X = Y = Cl or Br) as well as with CCl<sub>4</sub> (X = CCl<sub>3</sub>; Y = Cl), CBrCl<sub>3</sub> (X = CCl<sub>3</sub>; Y = Br) and N-bromosuccinimide (X = succinimidyl; Y = Br). Sulphuryl chloride reacts somewhat differently, since the SO<sub>2</sub>Cl radical formed in (2) decomposes to form a chlorine atom and SO<sub>2</sub>, at least in refluxing solvents, where the concentration of sulphur dioxide is low.<sup>9</sup> So far, the mechanism of free radical chlorinations with phosphorus pentachloride does not seem to have been investigated; this compound may react in (2) to form PCl<sub>4</sub>·, which then decomposes into PCl<sub>3</sub> and a chlorine atom continuing the chain.

### 1. The halogenation of norbornane

Conversions of norbornane were generally kept below 40 per cent in order to form mainly monohalides. Ultra-violet light, benzoyl peroxide or azoisobutyronitrile were used as the initiating agents. Working up was generally done by fractional distillation through an 8-plate column; after removal of hydrogen halide or chloroform and unreacted reagent, toluene was added as an entrainer to prevent clogging of the apparatus (m.p. norbornane 85°; b.p. 110°). Yields of monohalides based on halogenating agents converted (except N-bromosuccinimide) were generally high; dihalides were the only by-products detected.

<sup>3</sup> Personal communication, based on preliminary electron-diffraction studies, by Dr. H. Mendel of these Laboratories.

<sup>4</sup> J. D. Roberts, W. Bennett and R. Armstrong, *J. Amer. Chem. Soc.* **72**, 3329 (1950).

<sup>5</sup> S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *J. Amer. Chem. Soc.* **74**, 1127 (1952).

<sup>6</sup> R. T. Blickenstaff and H. B. Hass, *J. Amer. Chem. Soc.* **68**, 1413 (1946).

<sup>7</sup> J. D. Roberts, J. Urbanek and R. Armstrong, *J. Amer. Chem. Soc.* **71**, 3049 (1949).

<sup>8</sup> J. P. West and L. Schmerling, *J. Amer. Chem. Soc.* **72**, 3525 (1950).

<sup>9</sup> G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.* **77**, 4031 (1955).

The compositions of isomers in monochloride cuts (b.p. 52–53°/20 mm Hg) were determined by infra-red absorption spectrophotometry based on standard samples (the pure *exo*-2-chloride, 7-chloride containing some nortricycyl chloride, a mixture containing about 70 per cent of *endo*- and 30 per cent of *exo*-2-chloride). The infra-red analyses were supported by occasional solvolysis runs, *exo*-2-halides being solvolysed much more rapidly than the other isomers.<sup>4</sup> Gas-liquid chromatography failed to resolve the monochloride cuts; only a single peak was found in check runs with samples containing *exo*- and *endo*-2-chloride as well as 7-chloride. For the determination of *exo*-2-bromide, the infra-red bands found for the chloride were used; *endo*-2-bromide was not determined directly.

TABLE I. HALOGENATIONS OF NORBORNANE

Halogen donor	Initiator	Solvent	Temperature °C	Norbornyl chloride (%)*		
				<i>exo</i> -2	<i>endo</i> -2	7-
Cl <sub>2</sub>	u.v. light	CH <sub>2</sub> Cl <sub>2</sub>	42	70 (71)	25	2
Cl <sub>2</sub>	u.v. light	CCl <sub>4</sub>	40–50	73	22	†
Cl <sub>2</sub>	None	Gas phase	150	70 (71)	25	3
SO <sub>2</sub> Cl <sub>2</sub>	benzoyl peroxide	CH <sub>2</sub> Cl <sub>2</sub>	42	95	1–5	5
CCl <sub>4</sub>	benzoyl peroxide	CCl <sub>4</sub>	80	95	1–5	0
PCl <sub>5</sub>	u.v. light	CH <sub>2</sub> Cl <sub>2</sub>	42	95 (95)	1–5	5
PCl <sub>5</sub>	u.v. light	CCl <sub>4</sub>	80	95	1–5	3
PCl <sub>5</sub>	benzoyl peroxide	Chlorobenzene	105	90	†	†
Br <sub>2</sub>	u.v. light	CCl <sub>4</sub>	80	75†	†	†
CBrCl <sub>3</sub>	2:2'-azoisobutyronitrile	CBrCl <sub>3</sub>	80	98 (95)	†	†

\* The infra-red spectra gave no indications of the presence of other than 2- or 7-halides. Percentages given are based on infra-red spectra, the accuracy being probably better than 5 per cent. Values in brackets refer to percentages obtained by solvolysis.

† The remaining 25 per cent is probably *endo*-bromide.

‡ Not determined.

Chlorination with phosphorus pentachloride did not proceed satisfactorily when using benzoyl peroxide as the initiator at 80°. The difference between this result and successful chlorination at 105° may be due to a direct interaction of the initiator with PCl<sub>5</sub> without the formation of initiating radicals. Thus, at high temperatures and low peroxide concentrations, homolysis of the peroxide is sufficiently rapid to cause initiation; at the lower temperature, bi-molecular destruction of the peroxide prevails. This interpretation is supported by the fact that homolytic benzoyl peroxide decomposition is known to possess a high temperature coefficient (30 kcal) as well as by the smooth chlorinations with PCl<sub>5</sub> under the influence of ultra-violet light.

In the attempts to brominate norbornane with *N*-bromosuccinimide a dark brown colour was observed after ½ hr refluxing of the carbon tetrachloride solution. Some bromide, contaminated with bromoisobutyronitrile was formed, but could not be purified. It is believed that the small extent to which bromination did take place should be ascribed to free bromine formed rather than to the bromoimide. The procedure was followed which has been used by Ford and Waters for the bromination of cyclohexane.<sup>10</sup> A single experiment carried out with cyclohexane and

<sup>10</sup> M. C. Ford and W. A. Waters, *J. Chem. Soc.* 2240 (1952).

N-bromo-succinimide in carbon tetrachloride showed that here, too, a dark colour developed. Roberts *et al.* also failed to obtain a pure bromide when treating norbornane with the bromoimide.<sup>11</sup>

## 2. Competitive halogenations of cyclohexane and norbornane

These reactions were run in carbon tetrachloride or methylene chloride solution. Relative amounts of monohalides were determined by gas-liquid chromatography; the results were in good agreement with those obtained by isolation of the product.

TABLE 2. COMPETITIVE HALOGENATION OF NORBORNANE AND *cyclohexane* (molecular ratio 1 : 1)

Halogenating agent	Initiator	Solvent	Temperature °C	$\frac{k_{cyclohexane}^*}{k_{norbornane}}$
Cl <sub>2</sub>	u.v. light	CCl <sub>4</sub>	0-3	1.01 ± 0.05 (i : 1.00)
Cl <sub>2</sub>	u.v. light	CCl <sub>4</sub>	80	1.27 ± 0.05
SO <sub>2</sub> Cl <sub>2</sub>	benzoyl peroxide	CH <sub>2</sub> Cl <sub>2</sub>	42	1.31 ± 0.05
SO <sub>2</sub> Cl <sub>2</sub>	benzoyl peroxide	CCl <sub>4</sub>	50	1.35 ± 0.05 (i : 1.33)
CCl <sub>4</sub>	benzoyl peroxide	CCl <sub>4</sub>	80	1.42 ± 0.05
Br <sub>2</sub>	u.v. light	CCl <sub>4</sub>	0-5	0.98 ± 0.05
Br <sub>2</sub>	u.v. light	CCl <sub>4</sub>	80	1.79 ± 0.05
CBrCl <sub>3</sub>	2:2'-azoisobutyronitrile	CBrCl <sub>3</sub>	80	1.44 ± 0.05 (i : 1.40)

\* Mean values from 2-4 experiments (gas-liquid chromatography)

(i) Refers to values obtained by product isolation.

## DISCUSSION

### 1. Relative reactivities of the various positions in norbornane

If (1) is an irreversible process under the experimental conditions, the relative amounts of halides having their halogen atom attached to a certain carbon atom provide a reliable measure for the relative reactivity of that position towards the attacking species X· in (1). This is appreciably exothermic only for the cases in which X· is a chlorine atom; the back reaction may then be neglected.

With ·CCl<sub>3</sub>, (1) will be more nearly thermoneutral. Alkyl radicals are known to react more readily with CCl<sub>4</sub> or CBrCl<sub>3</sub> than with CHCl<sub>3</sub>, whereas the latter is present in very low proportion, and (1) will be practically irreversible.

Only in the case of bromination with Br<sub>2</sub> might the back reaction have a sufficiently low activation enthalpy to compete with the forward process. The only bromides detected were the 2-halides; it would seem unlikely that the 7- or 1-norbornyl radical, once formed, should preferentially attack HBr (to regenerate norbornane) rather than Br<sub>2</sub>. However, since no detailed study of the monobromides was made the possibility that small amounts of other bromides were present is not definitely excluded.

The occurrence of reactions of the type R'· + RH → R'H + R· can be neglected because of the relatively high activation enthalpies of such processes as compared with the reactions between R'· and halogen donor.

The 2-halides appear to be the main products in all cases (Table 1); only with Cl<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub> and PCl<sub>5</sub> was a small proportion of the 7-halide observed. This may be due

<sup>11</sup> J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, *J. Amer. Chem. Soc.* 72, 3116 (1950).

to the fact that the latter chlorinations involve the highly reactive and therefore non-selective chlorine atom in (1). With  $\text{CCl}_4$ , the abstraction step proceeds by the less reactive  $\cdot\text{CCl}_3$ .

The lower reactivity of the 7-position compared with the 2-positions is probably related to the decreased bond angle (1, 7, 4); formation of the 7-norbornyl radical should be resisted by a further increase of angle strain. In agreement with our halogenation results, methyl radicals react more slowly with methylene groups in cyclobutane than with those in cyclopentane or -hexane.<sup>12</sup>

The formation of bridgehead halides (1-chloride) could not be detected; their absence has not been definitely demonstrated, however. Here, formation of the radical would involve an appreciable increase of strain.

### 2. Relative reactivities of cyclohexane and norbornane

The  $k_c/k_n$  values recorded in Table 2 may be used for a comparison of the relative reactivities of a methylene group in cyclohexane and a 2-methylene group in norbornane. Since the four 2-methylene groups in the latter compound are responsible for about 95 per cent of the norbornyl halides, this comparison may be obtained multiplying  $k_c/k_n$  with  $2/3 \times 1/0.95$ .

The relative reactivities thus calculated are fairly close to unity (0.7–1.3), suggesting that the two types of methylene groups have comparable reactivities. The increases of  $k_c/k_n$  at increasing temperatures indicate, however, that the reaction with norbornane involves somewhat lower activation enthalpies, viz.  $\frac{1}{2}$ – $1\frac{1}{2}$  kcal, for all attacking radicals.\*

There are no *a priori* reasons for assuming that the exo- and endo-hydrogens will react at exactly the same rates; it should be noted, however, that sterical accessibilities will not be much different (cf. par. 3, Fig. D). Probably, the same radical will be formed when removing either the exo- or the endo-H atom; this radical will have a planar or near-planar configuration with regard to the three remaining valencies at C-2.

The similar reactivity and only slightly lower activation enthalpy for norbornane as compared with cyclohexane suggests that the 2-norbornyl radical is not appreciably stabilised by additional resonance as compared with the cyclohexyl radical. A similar conclusion was arrived at by Cristol and Brindell<sup>13</sup> on the basis of their studies on free radical initiated addition of *p*-thiocresol to norbornene. This is in contrast to the marked stabilisation through carbon-bridging which has been established for the 2-norbornyl cation.<sup>4,5</sup>

### 3. Exo-endo ratios

In the preceding section the assumption was made that only a single 2-norbornyl radical is formed when removing either the exo- or the endo-hydrogen atom. Assuming that this radical has a planar or near-planar configuration at the unsaturated centre, formation of either exo- or endo-isomers then depends on (2), the halogen donor attacking *either side of the plane*. Fig. C indicates that accessibility from the

\* The limited data available suggest that the lower activation enthalpies are counterbalanced by lower temperature-independent factors.

<sup>12</sup> A. F. Trotman-Dickenson, *Quart. Rev.* 7, 198 (1953).

<sup>13</sup> S. J. Cristol and G. D. Brindell, *J. Amer. Chem. Soc.* 76, 5699 (1954).

endo-side is less than that from the exo-direction because of the shielding effect of the methylene group in the 6-position. The difference should be the more significant the bulkier the halogen donor involved.

This expectation appears to be borne out by the experimental results. Thus, the small halogen molecules give appreciable proportions of endo-isomer, whereas the other reagents yield only small percentages. The latter results are in agreement with those of Roberts *et al.*,<sup>4</sup> who concluded that chlorination of norbornane with sulphuryl chloride gives 95 per cent of exo-2-chloride.\*

Similarly, addition of the bulky *p*-thiocresyl radical to norbornene-2 gives exclusively the exo-addition product.<sup>13</sup> Unfortunately, the stereochemistry of addition of "small" radicals to norbornene has not been investigated.

The fact that molecular chlorine gives the same exo-endo ratios at 0° and 80° (liquid phase) as well as at 150° (gas phase) suggests that these ratios are governed by temperature-independent factors rather than by differences in activation enthalpies in (2).

Finally, it should be noted that, in contrast to (2), the first step should hardly be affected by sterical factors because of the appreciable distance between the approaching reagent and the shielding methylene group in the 6-position (cf. Figs. C and D).

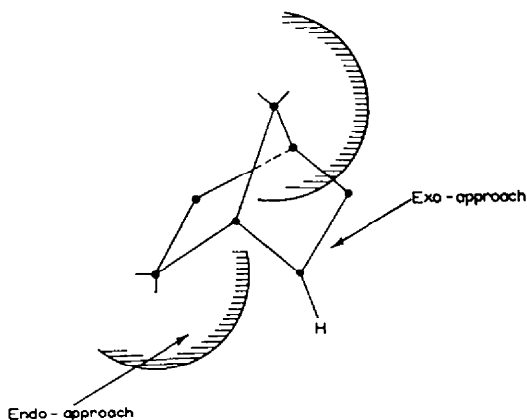


FIG. C. Shielding of endo side of 3(=2, 5 or 6)-norbornyl radical (schematically).

#### 4. Mechanisms of chlorination with $\text{PCl}_5$

The present data may be satisfactorily explained on the basis of our proposed scheme, which is analogous to that assumed for chlorinations with sulphuryl chloride. Since only a small proportion of endo-2-chloride is observed, it seems improbable that the reaction occurs through free chlorine, which might be formed from  $\text{PCl}_5$  by a reaction  $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$ . The operation of the reaction  $\text{PCl}_4 \cdot + \text{R}-\text{H} \rightarrow \text{R} \cdot + \text{PCl}_3 + \text{HCl}$  cannot be excluded; however, the formation of some 7-chloride suggests that the hydrogen abstracting agent in (1) is unselective, which may favour  $\text{Cl} \cdot$  rather than  $\text{PCl}_4 \cdot$ . Chain termination may proceed by a disproportionation reaction of  $\text{PCl}_4 \cdot$  forming a mixture of trichloride and pentachloride.

\* In a footnote to the paper by Roberts *et al.* cited above, the authors pointed out that this high degree of specificity was unusual, but no explanation was offered.

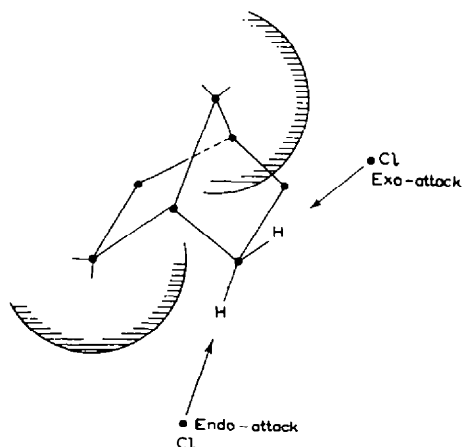


FIG. D. Illustration of minor differences in exo- or endo-attack at 3(=2, 5 or 6)-position in norbornane (schematically).

## EXPERIMENTAL

### 1. Preparation of norbornane

A steel high-pressure bomb (5 l.) was charged with freshly distilled commercial norbornadiene (450 g), b.p.  $89.5^\circ$ ,  $n_D^{20}$  1.4710, Ni-on-kieselguhr catalyst (23 g, 20% Ni) and hydrogen (35 atm). The bomb was set in rotation and slowly heated to  $110$ – $120^\circ$  ( $110^\circ$  after 1 hr). After 2 hr the pressure had fallen to 8 atm and the bomb was charged again with hydrogen to 60 atm. When the pressure had become constant (22 atm), the bomb was cooled, hydrogen allowed to escape and the solid contents diluted with pentane. The catalyst was removed by filtration and the filtrate shaken with sulphuric acid (96%) until the latter remained colourless. After washing with water, bicarbonate solution and again water, the pentane solution was dried over calcium chloride. Distillation yielded norbornane (347 g), b.p.  $105^\circ$  and m.p.  $85.5$ – $86^\circ$  (lit.<sup>1</sup> m.p.  $86$ – $87^\circ$ ).

### 2. Chlorination of norbornane

(a-1) *With Cl<sub>2</sub> in solution.* Norbornane (96 g, 1 mole) dissolved in methylene chloride (80 ml) was irradiated with ultra-violet light while a slow stream of chlorine was passed in during 5 hr. The reaction mixture was distilled through an 8-plate Vigreux column. After removal of the methylene chloride, norbornane (15 g) was collected at  $130^\circ$ . After cooling, toluene (87 g) was added to the residue and toluene and norbornane distilled together at  $145^\circ$ . The combined toluene fractions were 90 g. The distillation was continued at 20 mm, and chloride (46.4 g, 35.6%) collected, at  $52$ – $53^\circ$  which solidified at  $5.3$  to  $3.1^\circ$ ,  $n_D^{20}$  1.4851. (Found: Cl, 27.0; Calc. for C<sub>7</sub>H<sub>11</sub>Cl: Cl, 27.2%). In the literature the following physical constants are given for the isomeric monochloronorbornanes: exo-norbornyl chloride:  $n_D^{20}$  1.4849; m.p.  $-5$ <sup>14</sup> endo-norbornyl chloride:  $n_D^{25}$  1.4835; m.p.  $+28^\circ$  (containing about

<sup>14</sup> L. Schmerling, *J. Amer. Chem. Soc.* **68**, 195 (1946).

20% of exo-isomer);<sup>4</sup> 7-chloronorbornane:  $n_D^{25}$  1.4878 (containing about 15% of nortricycyl chloride).<sup>15</sup>

The distillation residue amounted to 8.3 g. The amount of norbornane in the toluene fractions was determined mass-spectrometrically to be 24.6 g. Some norbornane may have been lost owing to its high volatility. The yield of monochloride based on norbornane converted and lost (56.4 g) thus amounted to about 60%.

(a-2) *With Cl<sub>2</sub> in the gas phase.* A gaseous mixture of norbornane, benzene, chlorine and nitrogen (4 : 2 : 2 : 1) was passed at 150° through a Pyrex glass tube for 1 min. Benzene did not react under these conditions. The colourless liquid reaction mixture was collected and worked up as in (a-1). From norbornane (82 g), norbornyl chloride (37.9 g, 34.0%), b.p. 52–53°/20 mm;  $n_D^{20}$  1.4852, chlorine content 27.4%, solidifying at 6.0 to 3.9°. A higher-boiling liquid (7.7 g) was also formed.

An experiment carried out at 250° was unsuccessful owing to the deposition of carbon.

(b) *With SO<sub>2</sub>Cl<sub>2</sub>.* Norbornane (96 g, 1 mole) was dissolved in methylene chloride (80 ml) and SO<sub>2</sub>Cl<sub>2</sub> (34 g, 0.25 mole) together with benzoyl peroxide (0.25 g, 0.001 mole) added. The mixture was refluxed for 24 hr and yielded chloride (24.6 g, 19%), b.p. 52–53°/20 mm and solidifying at –4.8 to –6°;  $n_D^{20}$  1.4844. Norbornane (74 g) was recovered; distillation residue was 2.2 g, and yield of monochloride based on norbornane converted and lost (22 g) amounting to 83%.

(c) *With CCl<sub>4</sub>.* Norbornane (24 g, 0.25 mole) and benzoyl peroxide (3 g, 12.5 mole) were dissolved in carbon tetrachloride (100 ml) and the solution refluxed for 24 hr, and worked up according to (a-1) gave norbornyl chloride (8 g, 24.5%)  $n_D^{20}$  1.4845, m.p. –5 to –6°; residue (2 g); higher-boiling products did not appear to have been formed.

(d-1) *With PCl<sub>5</sub>.* A boiling solution of PCl<sub>5</sub> (52.1 g, 0.25 mole) and norbornane (48 g, 0.5 mole) in carbon tetrachloride (500 ml) was irradiated with ultra-violet light. After 31 and 55 hr, respectively, 73 and 98% of hydrogen chloride had been evolved.

The phosphorus trichloride and carbon tetrachloride were distilled and the residue fractionated *in vacuo*. Norbornyl chloride (15 g, 23.0%) were collected at 52–53°/20 mm;  $n_D^{20}$  1.4841; m.p. –5 to –6°. The residue amounted to 9.3 g.

The distillate of PCl<sub>3</sub> and CCl<sub>4</sub> was shaken with water for 3 hr, the total acid being determined by titration with alkali and chloride ion by Volhard titration. Thus PCl<sub>3</sub> (0.24 mole, 96%) were found in the distillate.

With the same quantities of reactants in boiling methylene chloride as the solvent, 31.4 and 89% of hydrogen chloride was evolved after 31 and 117 hr respectively, and PCl<sub>3</sub> (216.5 mmoles, 87%) was present in the distillate.

The yield of norbornyl chloride,  $n_D^{20}$  1.4843, m.p. –5 to –6° was 11 g (16.9%); the residue amounted to 7 g, containing PCl<sub>5</sub> (28 mmoles, 11.2%).

(d-2) *With PCl<sub>5</sub> and benzoyl peroxide.* A solution of norbornane (24 g, 0.25 mole), PCl<sub>5</sub> (26 g, 0.125 mole) and benzoyl peroxide (1.8 g, 0.007 mole) in chlorobenzene (150 ml) was stirred and at 100–105° a smooth reaction took place. After 45 min hydrogen chloride (0.108 mole) had been evolved and the reaction was complete after 1½ hr. Phosphorus trichloride was distilled, toluene (40 ml) added and the mixture fractionated carefully. Norbornyl chloride (6.9 g, 0.053 mole, 21.2%) were collected,

<sup>5</sup> J. D. Roberts, F. O. Johnson and R. A. Carboni, *J. Amer. Chem. Soc.* **76**, 5692 (1954).



b.p. 84–88°/76 mm,  $n_D^{20}$  1.4848 with a chlorine content 26.9% (calc. 27.2%) and solidifying between –5° and –10°.

### 3. Bromination of norbornane

(a) *With bromine.* To a solution of norbornane (36 g, 0.38 mole) in boiling carbon tetrachloride (100 ml), bromine (18 g, 0.11 mole) was gradually added under irradiation with ultra-violet light. At the end of the reaction, the reaction mixture was slightly yellow, and worked up in accordance with the chlorination experiments. Norbornyl bromide (12.7 g, 25.6%) was collected at 68–70°/17 mm,  $n_D^{20}$  1.5147; and residue (2.8 g) remained. (Found: C, 48.1; H, 6.5; Br, 45.6; Calc. for  $C_7H_{11}Br$ : C, 48.02; H, 6.33; Br 45.7%.) In the literature the following physical constants are given for the isomeric monobromonorbornanes: exo-norbornyl bromide: b.p. 84–87°/31 mm,  $n_D^{25}$  1.5126;<sup>11</sup> endo-norbornyl bromide: b.p. 70°/15 mm,  $n_D^{25}$  1.5198.<sup>4</sup>

(b) *With  $CBrCl_3$  and azoisobutyronitrile.* A solution of norbornane (12 g, 125 mmoles) and 2:2-azoisobutyronitrile (0.98 g, 6 mmoles) in bromotrichloromethane (105 g) was kept at 80° for 24 hr.

After removal of chloroform and bromotrichloromethane at 100 mm, the residue was cooled to –15°; a solid separated which after crystallisation from methanol, had m.p. 185–186° and mixed m.p. with hexachloroethane 186° (closed capillary).

Distillation of the residue at 20 mm afforded norbornyl bromide (5.2 g) which by mass-spectrometrical analysis was shown to contain 15% hexachloroethane. Infra-red analysis showed 84% exo-norbornyl bromide to be present.

(c) *With N-bromosuccinimide.* To a solution of norbornane (24 g, 0.25 mole) in carbon tetrachloride (200 ml), N-bromosuccinimide (18 g, 0.1 mol) and 2:2'-azoisobutyronitrile (0.25 g, 1.5 mmoles) were added and the mixture was gently refluxed. The bromosuccinimide dissolved slowly, after 35 min a slightly yellow colour developed and succinimide precipitated. Then the colour of the reaction mixture turned to brown, possibly owing to the formation of free bromine. The brown colour subsequently changed to light yellow and after 16 hr refluxing a black deposit was present on the bottom of the reaction vessel. Distillation gave an impure bromide (3.5 g), which from its infra-red spectrum appeared to contain some bromoisobutyronitrile. Pure norbornyl bromide could not be isolated; the amount of exo-isomer could not be determined in the impure product.

### 4. Competitive halogenations of norbornane and cyclohexane

A solution of cyclohexane (4.21 g, 50 mmoles) and norbornane (4.783 g, 50 mmoles) in carbon tetrachloride (50 ml) was boiled under reflux and a solution of chlorine (10 mmoles) in carbon tetrachloride (50 ml) was injected in the bottom of the reaction vessel under irradiation with ultra-violet light.

At the end of the reaction, the hydrogen chloride and carbon tetrachloride were removed *in vacuo* leaving a residue (20 ml). This residue was analysed by gas-liquid chromatography employing a column of dinitrodiphenic  $C_5 - C_6$  ester on Sterchamol at 120° with  $\beta$ -ray detection in hydrogen as the carrier gas.<sup>18</sup> A heat conductance cell could not be used for detection owing to decomposition of the chlorides on the platinum wire and subsequent corrosion of the wire by the chlorine formed.

<sup>18</sup> A. I. M. Keulemans, *Gas Chromatography*. Reinhold, New York (1957).

The G.L.C. analysis showed the monochlorides to contain norbornyl chloride (45% molar) cyclohexyl chloride, (55% molar), hence,

$$\frac{k_e}{k_n} = \frac{\log\left(1 - \frac{5.5}{50}\right)}{\log\left(1 - \frac{4.5}{50}\right)} = 1.27.$$

All our competition experiments were carried out in an analogous manner; sulphuryl chloride chlorinations were initiated by benzoyl peroxide, so was the chlorination by carbon tetrachloride. The bromination with bromotrichloromethane was initiated by 2:2'-azoisobutyronitrile. In the latter experiment the bromotrichloromethane was completely removed from the reaction mixture before G.L.C. analysis, by codistillation at 100 mm with toluene until the distillate had the refraction of pure toluene.

### 5. *Infra-red spectroscopic measurements*

Infra-red spectra were determined in a Grubb-Parson double beam spectrometer from 2 to 15  $\mu$ , and in a Perkin-Elmer 112 spectrometer from 15 to 25  $\mu$ .

Contents of exo-2-chloronorbornane were calculated on the basis of the spectrum of the pure exo-compound, using the absorption bands at 8.76 and 17.05  $\mu$ . Comparison of the results indicated that the latter band is most trustworthy. For the determination of exo-bromonorbornane the same absorption bands were used; with the bromonorbornanes no contents of endo-isomer were determined, only the pure exo-compound being available as a standard.

For the determination of endo-chloride contents the absorption bands at 11.56, 10.02 and 9.38  $\mu$  were used. In the standard compound, which consisted of exo- and endo-2-chloronorbornane, the amount of endo-isomer was calculated from the band at 22.12  $\mu$ .

Comparison of the spectra with that of 7-chloronorbornane showed that this isomer was present in all mixtures, except in that obtained in the benzoyl peroxide initiated chlorination with  $\text{CCl}_4$ .

The spectra of all mixtures showed absorption bands which cannot be attributed to the exo-2-, endo-2- or 7-chloride. In view of the complicated spectra and the low intensities of these bands, a definite identification was not possible.

### 6. *Solvolysis of norbornyl chlorides*

Solvolysis experiments according to the method of Brown and Fletcher<sup>17</sup> were carried out in 70% aqueous ethanol at 70°. Since the solvolysis rates of endo-2- and 7-chloronorbornane are very low as compared with that of the exo-2-chloride,<sup>4,15</sup> the amount of the exo-isomer could be calculated from a plot of  $\log(a-x)$  against time.

At 70°, for the pure exo-2-chloride a first-order rate constant  $3.47 \times 10^{-5} \text{ sec}^{-1}$  was found up to a conversion of over 98%; the first-order constant for the endo-chloride, derived from the last part of the solvolysis plot of a 75 : 25 mixture of endo- and exo-chloride, was found to be  $2.5 \times 10^{-7} \text{ sec}^{-1}$ .

<sup>17</sup> H. C. Brown and R. S. Fletcher, *J. Amer. Chem. Soc.* **71**, 1845 (1949).

In all cases the data obtained in solvolysis experiments agreed very well with the results of infra-red measurements.

### 7. Preparation of standard compounds for infra-red spectroscopic measurements and solvolysis

(a) *Exo-2-chloronorbornane* was prepared according to Schmerling,<sup>14</sup> by addition of HCl to norbornene. After working-up by fractional distillation pure *exo-2-chloride* (87%) was obtained, b.p. 55.5°/21 mm, m.p. -5°,  $n_D^{20}$  1.4844. The solvolysis of this product at 70° in ethanol (70%) proceeded by a first-order reaction to over 98%, with  $k_1 = 3.47 \times 10^{-5} \text{ sec}^{-1}$  from the chloride (8.16 mmoles) HCl (8.15 mmoles) were formed.

(b) *Exo-2-bromonorbornane* was prepared according to Roberts *et al.*<sup>11</sup> by addition of HBr to norbornene. The yield of the crude 2-bromonorbornane, b.p. 84-87°/31 mm, was 77%. Fractional distillation in a 35 cm Vigreux column gave pure *exo-2-bromonorbornane* (72%) b.p. 82°/29 mm,  $n_D^{25}$  1.5126,  $d_D^{25}$  1.3808.

(c) *Endo-2-chloronorbornane*. Diels-Alder addition of vinyl chloride to *cyclopentadiene* and subsequent catalytic hydrogenation gave a norbornyl chloride which consisted of *endo-2-chloride* (60%) and *exo-2-chloride* (40%), according to infra-red spectroscopic analysis in comparison with the pure *exo*-compound.

The above chloride (10 g) were refluxed for 16 hr in a solution of  $\text{Na}_2\text{CO}_3$  (2g) in water (20 ml) and acetone (25 ml). After addition of more water, ether extraction and drying and evaporation of the ether, the semi-solid residue was percolated over silica with pentane elution. Evaporation of the pentane and fractional distillation gave monochloride (3.4 g) b.p. 79°/48 mm, m.p. 30.1-30.5°.

Solvolysis of the above compound according to Brown and Fletcher<sup>17</sup> showed it to consist of 73% *endo*- and 27% *exo*-isomer. This was confirmed by infra-red spectroscopic analysis, which indicated the presence of 25-30% *exo*-compound.

(d) *7-chloronorbornane* was synthesised according to Roberts *et al.*<sup>15</sup> by pyrolysis of *syn-7-chloro-exo-norbornyl-2-naphthoate* and catalytic hydrogenation of the resulting *syn-7-chloronorbornene*. On fractional distillation, two fractions with b.p. 91°/8.5 mm were obtained; the first, 0.7 g,  $n_D^{20}$  1.4827, was partly solid at room temperature; the second, 1.0 g,  $n_D^{20}$  1.4866, solidified at about 0°. The latter fraction was used as a standard compound in spectroscopic measurements; its infra-red spectrum agreed with that given by Roberts, showing that it also contained 15-20% of nortricycyl chloride.