The Mechanism of the Addition of Chlorine to Olefins with Iodobenzene Dichloride

DENNIS D. TANNER AND GEOFFREY C. GIDLEY[1]

Department of Chemistry, University of Alberta, Edmonton, Alberta

Received June 13, 1967

The reaction of iodobenzene dichloride with norbornene at temperatures ranging from −20 to 80° has been shown to react by two distinguishable and controllable mechanistic pathways. A free-radical chain addition of chloride to norbornene yields as the sole chlorinated products *trans*-2,3-dichloronorbornane (74%) and *exo,cis*-2,3-dichloronorbornane (26%). The *exo,cis* dichloride has been shown to arrive from this free-radical reaction and not from a *cis* molecular addition as had been previously proposed. Molecular oxygen has been shown to inhibit efficiently the radical chain reaction and a slower ionic addition of chlorine to the double bond takes place leading to *exo*-2-*syn*-7-dichloronorbornane and nortricycyl chloride, the same products produced from the ionic addition of molecular chlorine to norbornene.

The addition of chlorine to olefinic double bonds using iodobenzene dichloride (IBD) as a halogenating agent has received attention from several groups of workers. Bloomfield[2] reported that the chlorination of solutions of natural rubber with IBD in refluxing carbon tetrachloride gave a nearly quantitative addition product, while the addition of hydroquinone was shown to inhibit the halogenation reaction. From these inhibition experiments he concluded that a free-radical chain halogenation process was involved. These experiments were later repeated by another group of workers[3] who substantiated Bloomfield's observations.

The addition of chlorine to cholesteryl benzoate with IBD in refluxing carbon tetrachloride was reported to give excellent yields of halogenated olefins.[4] The composition of the halogenation mixture was shown to consist of two of the four possible isomeric dichlorides. Addition of molecular chlorine to cholesteryl benzoate under the same conditions yielded only one of the isomeric chlorides, but a mixture of other unidentified products was also obtained.

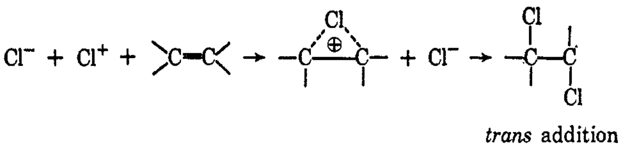
Barton and Miller[5] studied the stereochemistry of the cholesteryl benzoate chlorination and found that molecular chlorine gave *trans*-5α,6β-dichlorocholestan-3β-yl benzoate while IBD halogenation yielded the *trans*-5α,6β and the *cis*-5α,6α isomers. These workers proposed that two mechanisms were involved in IBD halogenation, the first and ionic reaction which is facilitated by the presence of water (Scheme I) and the second, a molecular addition to yield the *cis* addition product (Scheme II).

Cristol, Stermitz, and Ramey[6] found that, in the presence of 2,4,6-trinitrobenzene, IBD halogenated acenaphthylene in refluxing chloroform to give a 28% yield of the *trans* addition product, while molecular chlorine gave low yields of the *cis* isomer.

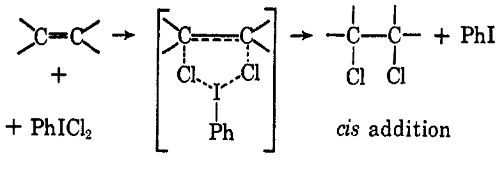
Summerbell and Lunk[7] halogenated *p*-dioxene with both IBD and molecular chlorine and reported that molecular chlorine yielded 61% *cis* and 39% *trans* addition product while the same substrate with IBD in refluxing carbon tetrachloride yielded 5% *cis* isomer and 95% *trans* addition products.

SCHEME I

$PhICl_2 + H_2O \rightarrow HOCl + H^+\ Cl^- + PhI$



SCHEME II



Poutsma[8] in a detailed study of the radical and ionic chlorination of norbornene with molecular chlorine obtained minor amounts of *exo,cis*-2,3-dichloronorbornane as one of the reaction products. In order to prepare this dichloride he treated IBD with norbornene and reported that the two major products from the reaction in refluxing carbon tetrachloride were *trans*-2,3-dichloronorbornane and *cis,exo*-2,3-dichloroborbornane.

Recent studies in this laboratory[9] on the halogenation reactions of IBD with saturated hydrocarbons have confirmed the free-radical chain mechanism proposed for IBD halogenation initiated thermally or photochemically.[10,11]

These studies coupled with the findings reported by Poutsma[8] have prompted us to reinvestigate the halogen addition reactions of IBD in light of a free-radical chain process.

Results

The addition of chlorine to norbornene (I) using IBD as the halogenating reagent gave products resulting from ionic addition–rearrangement or free-radical addition, without rearrangement, depending upon the conditions under which the reactions were carried out (see Table I). At temperatures ranging from −20 to 80° in the absence of atomospheric amounts of oxygen the photoinitiated reaction of IBD with norbornene gave, in high yields (see Table II), only iodobenzene, *trans*-2,3-dichloronorbornane (II) (74%), and *exo,cis*-2,3-dichloronorbornane (III) (26%).

---

[1] University of Alberta Postdoctoral Fellow, 1966–1967.

[2] G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

[3] C. S. Ramakrishnan, D. Raghunath, and J. B. Pande, *Trans. Inst. Rubber Ind.*, **30**, 129 (1954); *Chem. Abstr.*, **49**, 657a (1955); *Rubber Chem. Technol.*, **28**, 598 (1955); *Chem. Abstr.*, **49**, 16493d (1955).

[4] C. J. Berg and E. S. Wallis, *J. Biol. Chem.*, **162**, 683 (1946).

[5] D. H. R. Barton and E. Miller, *J. Am. Chem. Soc.*, **72**, 370 (1950).

[6] S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *ibid.*, **78**, 4939 (1956).

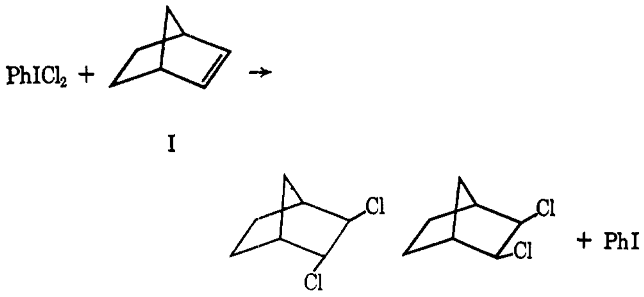
[7] R. K. Summerbell and L. C. Lunk, *ibid.*, **79**, 4802 (1957).

[8] Marvin L. Poutsma, *ibid.*, **87**, 4293 (1965).

[9] D. D. Tanner and P. B. Van Bostelen, *J. Org. Chem.*, **32**, 1517 (1967).

[10] G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

[11] D. F. Banks, E. S. Huyser, and J. Kleinburg, *J. Org. Chem.*, **29**, 3692 (1964).



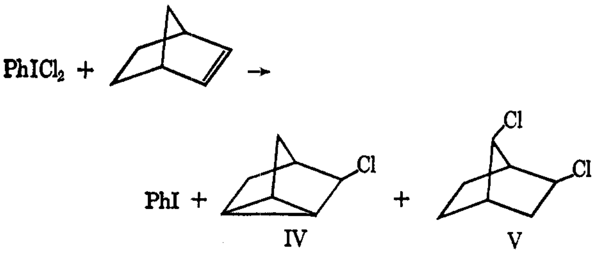
I

II III

This reaction was initiated by irradiation at −20° to 80° (reactions 1–7, 14–22, 34–36, 42,44, 46–48) or thermally (reactions 30–33, 39, 43, 45–59) at temperatures ranging from 40 to 80°. The ratio of these addition products, II:III, was found to be constant, within experimental error, over the entire range of temperatures studied. The addition of trace amounts, (3%), of *sym*-trinitrobenzene at 0° (reactions 15 and 16) or hydroquinone at 40° (reaction 34) was shown to inhibit the reaction while the product ratio of II:III was found to remain constant. *sym*-Tri-*t*-butylphenol at 0° (reaction 14), hydroquinone at 80° (reaction 42), AIBN at 40° (reactions 32 and 33), or benzoyl peroxide at 80° (reaction 45) seemed to have no effect on the length of time required for complete reaction nor were the product ratios affected. The addition of equimolar amounts of water to the reaction mixture (reaction 35) was shown not to affect the path of the reaction.

When the reaction between norbornene (10 mmoles), and IBD (5 mmoles) was carried out, in the usual manner, refluxing carbon tetrachloride (25 ml) in flasks which were open to atmospheric oxygen, the products obtained were mainly the isomeric dichlorides II and III and small amounts (7–10%) of two other chlorinated norbornyl compounds, IV and V (reactions 46–49).

The course of the reaction was dramatically changed over the range 0 to 80° in the presence of atmospheric amounts of molecular oxygen (reactions 8, 9, 24–27, 29, 37, 38). Both thermal (reactions 12, 13, 23, 24, 25, 40, 41) and photoinitiated (reactions 8, 9, 26–28, 37, 38) reactions were inhibited by molecular oxygen and the halogenation products from these reactions were found to be almost exclusively at the lower temperatures the products predicted for the ionic halogenation of norbornene, nortricyclyl chloride (IV) and *exo*-2-*syn*-7-dichloronorbornane (V) (eq 1). Small amounts

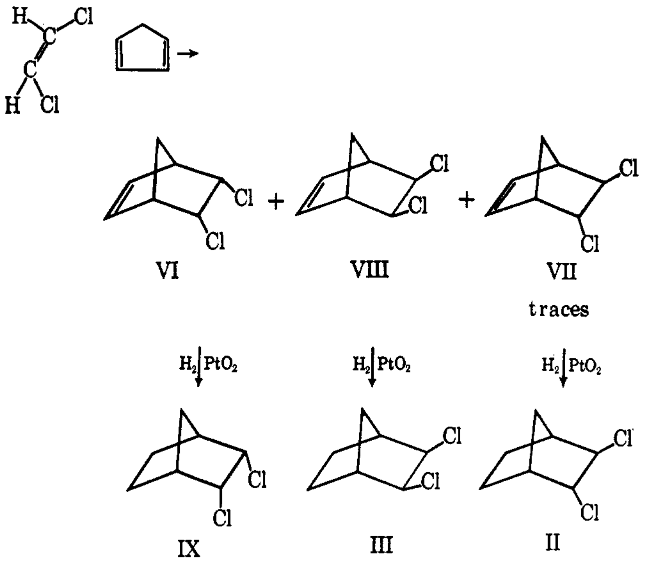


IV V (1)

of the radical addition products II and III (9–35%) were also found (reactions 8, 9, 26–27) accompanying the two major products. The yield from the oxygen-inhibited reactions were characteristically low since the products from the concomitant rearrangement of IBD itself[9,12] were always present in significant amounts (>50%); see Table II.

The Diels–Alder reaction between *cis*-dichloroethene and cyclopentadiene has been reported to give *endo*,-*cis*-5,6-dichloronorbornene (VI), traces of *trans*-5,6-dichloronorbornene (VII),[12] and *cis,exo*-5,6-norbornene (VIII).[8] Upon repetition of this reaction we were able to show by glpc analysis the presence of VIII in approximately 30% yield. Upon isolation by fractional distillation and preparative glpc VIII was assigned the structure of *exo,cis*-5,6-dichloronorbornene on the basis of its nmr spectrum. Upon catalytic hydrogenation, VIII was converted to dichloride III, the same dichlorinated isomer which was isolated by Poutsma[8] from the reaction of IBD and norbornene. Isomer III was shown by nmr and infrared spectra to be the same dihalide isolated by us from the reaction of IBD with norbornene in the absence of molecular oxygen. (See Scheme III.)

SCHEME III



VI VIII VII

traces

IX III II

Compounds IV, V, II, and IX were synthesized according to the method of Roberts, *et al.*[13] These independently synthesized compounds had infrared spectra and refractive indices and/or melting points which were identical with those of the known halides. The nmr spectra of IX[14,8] and II[8] were those of the reported compounds, and the nmr spectra of IV and V, not previously reported, were consistent with the assigned structures. Product VIII, isolated from the Diels–Alder reaction of *cis*-dichloroethene and cyclopentadiene, the unsaturated precursor of III, gave a nmr spectra different from that reported for VI,[15] but consistent with the spectrum of a *cis* dichlorinated norbornene, τ 3.86, 6.08, 7.04, and 7.6–8.8, which was contaminated with a small amount of VI. The absorption intensities were 2.8:2.4:2.0:3.2 and glpc analysis showed contamination with VI. Upon catalytic hydrogenation VIII was converted to III which was isolated in pure form by preparative glpc.

---

[12] Results of unpublished work from this laboratory on the thermal and photochemical rearrangement of IBD.

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

[14] P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

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

TABLE I
REACTION OF NORBORNENE WITH IODOBENZENE DICHLORIDE

Reacn no.	Conditions[a]	Temp, °C	Time,[b] hr	Product analysis, %[c,d]				Ratio of II/III
				II	III	IV	V	
1		−20	5	77.3	22.7			3.4
2		−20	5	73.2	26.8			2.7
3		0	4	76.3	23.7			3.2
4		0	2	72.8	27.2			2.7
5		0	4	70.5	29.5			2.4
6		0	4.5	77.2	22.4			3.4
7		0	4.5	73.2	25.9			2.8
8	+ oxygen	0	44	26.2	9.3	46.5	18.0	2.8
9	+ oxygen	0	47	7.0	2.0	79.0	12.0	3.5
10	Dark	0	>196[o]					
11	Dark	0	>196[o]					
12	Dark + oxygen	0	>196[o]					
13	Dark + oxygen	0	>196[o]					
14	+ phenol[e]	0	5–6	73.5	26.5			2.8
15	+ TNB[f]	0	17	73.0	27.0			2.7
16	+ TNB[f]	0	17	74.6	25.4			2.9
17		25	0.75	72.8	27.2			2.7
18		25	0.75	75.9	24.1			3.1
19		40	0.33	75.2	24.8			3.0
20		40	0.33	75.9	24.1			3.1
21		40	0.33	73.5	26.4			2.8
22		40	0.33	71.7	28.3			2.5
23	Dark + oxygen	40	>96					
24	Dark + oxygen	40	222	33.0	16.0	35.0	16.0	2.1
25	Dark + oxygen	40	222	43	13	38	6	3.3
26	+ oxygen	40	>14	25	10	33	32	2.5
27	+ oxygen	40	>14	20	6	70	4	3.3
28	+ oxygen	40	19					
29	Dark + oxygen + water	40	>96	37	12	44	7	3.1
30	Dark	40	5–6	74.1	25.9			2.9
31	Dark	40	5–6	74.4	25.6			2.9
32	Dark + AIBN[h]	40	5–6	72.4	27.6			2.6
33	Dark + AIBN[h]	40	5–6	73.4	26.6			2.8
34	+ phenol[g]	40	1.5	70.3	29.7			2.4
35	+ water	40	1.15	76.2	23.8			3.2
36		74	0.04	73.6	26.4			2.8
37	+ oxygen	81	1.5	66.0	22.4	11.6	*j*	2.9
38	+ oxygen	81	1.5	66.4	22.8	10.8	*j*	2.9
39	Dark	76	0.04	75.4	24.6			3.1
40	Dark + oxygen	80	>2	58.0	25.0	16.0	1.0	2.4
41	Dark + oxygen	80	>2	62.2	20.6	15.4	2.0	3.0
42	+ phenol[g]	78	0.04	75.0	25.0			3.0
43	Dark + phenol[g]	78	0.04	73.0	27.0			2.7
44	+ peroxide[i]	78	0.04	67.0	33.0			2.0
45	Dark + peroxide[i]	78	0.04	72.0	28.0			2.6
46	+ phenol[k,n]	78	2	67	26	7	*j*	2.6
47	+ TNB[k,l]	78	2	72	26	2	*j*	2.8
48	+ oxygen[k,m]	78	2	66	24	6	4	2.8
49	Dark[k]	78	2	71.6	28.4			2.5

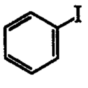
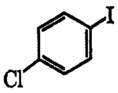
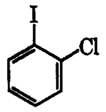
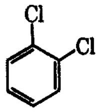
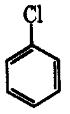
[a] All reactions were carried out in irradiated, degassed carbon tetrachloride solutions of norbornene (0.15–0.8 *M*) and iodobenzene dichloride (0.13–0.20 mmole/ml) unless otherwise indicated. [b] Times were taken from first immersion of reaction tube in constant-temperature bath to the appearance of a clear reaction mixture. [c] Percentages expressed relative to proportion of chlorinated norbornanes only. [d] In those reactions in which there was participation by the ionic mechanism, the products from the rearrangement of iodobenzene dichloride were also found (*o*-chloroiodobenzene, *p*-chloroiodobenzene, *o*-dichlorobenzene, chlorobenzene). Iodobenzene was formed in all reactions. [e] *sym*-Tri-*t*-butylphenol (3.6×10^{-3} *M*). [f] *sym*-Trinitrobenzene (3.6×10^{-3} *M*). [g] Hydroquinone (3.6×10^{-3} *M*). [h] 2,2′-Azobis(2-methyl propionitrile) (3.6×10^{-3} *M*). [i] Benzoyl peroxide (3.6×10^{-3} *M*). [j] In these reactions the glpc traces were run under conditions where V was not resolved. [k] A preparative-scale reaction. Norbornene (1.0×10^{-2} mole) and iodobenzene dichloride (5.0×10^{-3} mole) in refluxing carbon tetrachloride (25 ml). [l] As K plus *sym*-trinitrobenzene (1.5×10^{-4} mole). [m] As K with air bubbled through the refluxing solution. [n] As K plus hydroquinone (1.5×10^{-4} mole). [o] Only 29–39% reaction after 196 hr by iodometric titration.

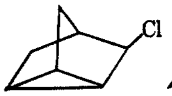
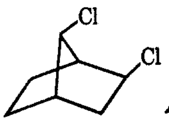
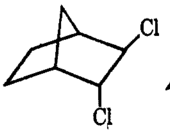
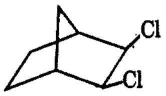
Compound III gave the same nmr spectra, reported by Poutsma[8] for the *cis,exo* isomer.

The halogenated products IV, V, III, and II were all isolated from typical reaction mixtures of IBD and norbornene by preparative glpc and the isolated products were shown by their infrared and nmr spectrum to be identical with the authentic materials. The analyses of the reaction mixtures were performed by glpc and the identity of the products of these analyses were confirmed by comparison of their retention times with those of the authentic materials on two different glpc columns.

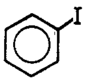
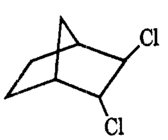
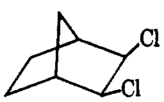
TABLE II

Products of the Reaction of Norbornene with IBD in the Presence of Molecular Oxygen at 40° [a]

IBD					
2.7	0.93	0.32	0.52	0.05	0.04

			
0.62	0.04	0.18	0.05

Products of the Photoinitiated Reaction of Norbornene with IBD AT 40° [b]

IBD				% yield of dichlorides
2.81	2.73	2.15	0.85	106%
2.54	2.31	1.75	0.66	98%

[a] See Table I, reactions 26 and 27. [b] See Table I, reactions 21 and 22.

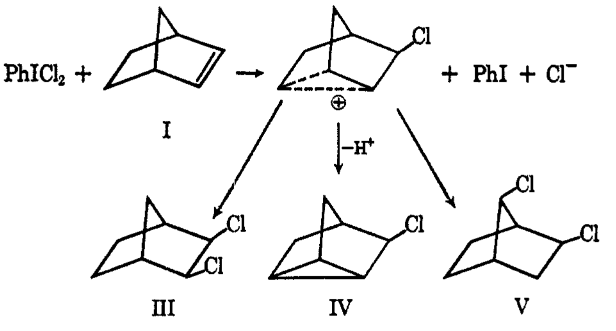
In the reactions inhibited by oxygen at 0° the major halogenated alkanes were shown to be IV and V (65–92%), while minor amounts of II and III (8–35%) could be found.

Discussion

Investigation of the reaction of the bicyclic olefin norbornene with IBD affords the opportunity to differentiate between the three halogenation mechanisms previously proposed for this chlorinating reagent.

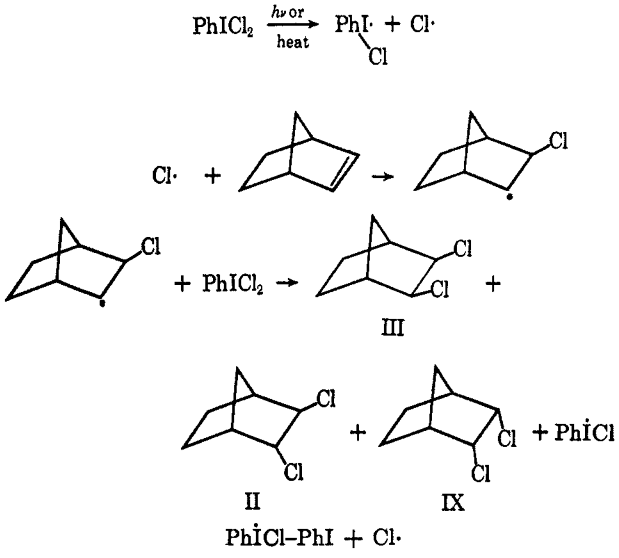
The ionic reaction of norbornene with molecular chlorine gave two major products, *syn*-7-*exo*-2-dichloronorbornane (V) and nortricyclyl chloride (IV),[8,13] in greater than 90% yield. These products would be expected from an ionic reaction if IBD with that olefin, reaction Scheme IV.

SCHEME IV



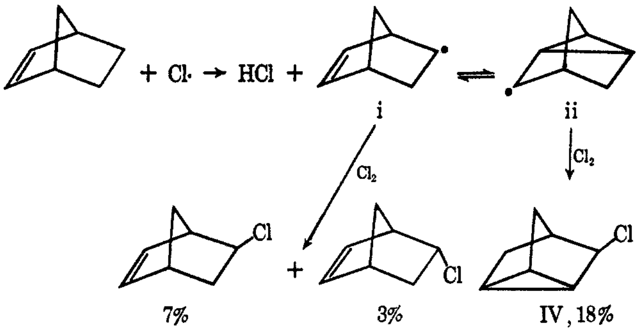
Free-radical reactions of norbornene and other bicyclic olefins lead exclusively to nonrearranged addition products.[16,8] The predicted products from the radical addition to norbornene can be seen in Scheme V.

SCHEME V



In his study of the chlorination of norbornene[8] Poutsma, extrapolating from his experimental data, suggested that the "pure" radical halogenation of norbornene should yield, in addition to III and II, appreciable amounts of products derived from radical abstraction by atomic chlorine (Scheme VI).

SCHEME VI



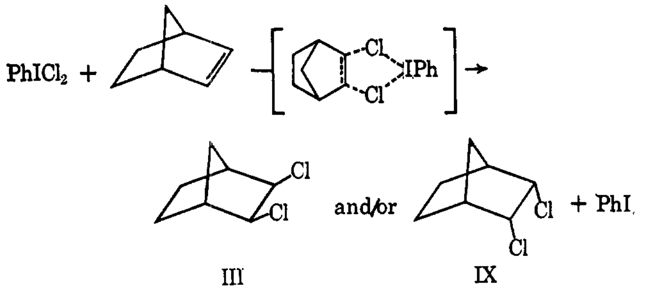
Normally hydrogen abstraction reactions of IBD proceed through a radical chain sequence where PhİCl is the chain carrying species.[9,11] In the chain mechanism proposed for halogen addition to olefins with IBD, chlorine atoms are the chain-propagating radicals. Any successful competition between abstraction and addition by the atomic chlorine would evidence itself by the production of substitution products; furthermore the insolubility of the halogen-transfer reagent, especially at low temperatures, would greatly favor the isomerization of i to ii and the subsequent formation of IV, if indeed chlorine atom abstraction does take place under free-radical conditions. Since no detectable amount of IV was observed in the IBD halogenation of norbornene under free-radical conditions; abstraction reactions, Scheme V, do not appear to have been important. The inability of chlorine atoms, under our conditions, to abstract hydrogen rather than add to the olefinic double bond is in disagreement with the results found by Poutsma.[8] Conceivably, complex formation other than the iodonium radical, of the type investigated by Russell[10] for other aromatic solvents, between chlorine and iodobenzene could stabilize the halogen atom sufficiently to prevent abstraction processes from taking place.

A molecular addition process as that proposed by

---

[16] D. I. Davies and S. J. Cristol in "Advances in Free-Radical Chemistry," Vol. I, G. H. Williams, Ed., Logos Press Ltd., Academic Press, London, 1965, pp 159–169.

Barton and Miller[5] would be expected to give either or both of the two *cis* unrearranged products, III and IX.



Free-Radical Addition Reactions.—Thermally initiated and photoinitiated reactions of IBD with norbornene in the absence of molecular oxygen lead to the products predicted for free-radical halogenation, II and III, Scheme V. Inhibition of the rate of these reactions with trace amounts of hydroquinone, *sym*-trinitrobenzene, and molecular oxygen confirms the chain nature of the reaction, as written in Scheme V. The inhibition of radical chain addition was so complete with atmospheric amounts of molecular oxygen at 0° that the ionic reaction, *i.e.*, the slower formation of IV and V, was dominant (65–92%). When the reaction was carried out at 80° in carbon tetrachloride in the usual manner, under reflux in a flask open to atmospheric oxygen, the products were still predominantly those from the radical addition (see reactions 46, 47, 48). Presumably, because of the low solubility of oxygen in carbon tetrachloride at this temperature, the effect of oxygen is negligible in determining the mode of reaction, although some inhibition was noted even at these concentrations.

The *trans* addition product of IBD to acenaphthylene obtained by Cristol, *et al.*, may be interpreted as the product produced from free-radical addition, since the product obtained from the addition of molecular chlorine was the *cis* isomer. Presumably the inhibitor, *sym*-trinitrobenzene, used by these workers may not have inhibited the radical addition, but only effected the inhibition of the known facile radical promoted polymerization of acenaphthene.[17]

The chlorination of cholesteryl benzoate with molecular chlorine or with IBD and large amounts of added water was shown by Barton[5] to give *trans* addition. If *trans* addition is the result of ionic halogenation of cholesteryl benzoate, then the *cis* addition product, obtained when the chlorination is carried out under conditions which gave us the products attributed to free-radical addition, may well have been the normal product from homolytic addition to cholesteryl benzoate and not the proposed molecular *cis* addition process.

In the reaction of norbornene with IBD, it was conceivable that the product of radical addition was solely the *trans* dichloride, II, and that the *cis* dihalide, III, arose from a *cis* molecular addition. Molecular oxygen, *sym*-trinitrobenzene, and hydroquinone were shown to inhibit the formation of both II and III equally. This would not be the result if the formation of both products were not both due to a free-radical chain process. The observation, in the case of *sym*-trinitrobenzene or hydroquinone inhibition, that although the formation of both II and III was retarded their product ratios remained the same as for the uninhibited reactions, clearly ruled out the occurrence of a *cis* molecular addition. Furthermore, the invariance of the ratios of II/III over the range of temperatures studied strongly suggests that both products are formed by reactions having similar entropies of activation. This would not be likely for products arising from a free-radical and a molecular mechanism.

Ionic Addition Reactions.—In sealed ampoules in the presence of molecular oxygen the thermal or photoinitiated, free-radical chain reaction of IBD and norbornane was strongly inhibited and the slower ionic process began to determine the course of the reaction, see Scheme IV. The products of norbornene halogenation from this reaction being primarily, at least at lower temperatures, the rearranged dichloride V and nortricyclyl chloride IV. During the course of the ionic halogenation the rearrangement of IBD itself competes with the halogenation of norbornene and low overall yields of IV and V resulted.[12]

Photoinitiated reactions inhibited by molecular oxygen, to give ionic products IV and V, gave low yields of chlorinated norbornene. The rate of the radical rearrangement reaction of IBD did not seem to be greatly affected by oxygen and therefore light did lead to the disappearance of IBD through the product of these photorearrangement products. The competition between the photorearrangement and the ionic addition was more pronounced at lower temperatures.

Experimental Section

Materials.—Commercial norbornene (Aldrich Chemical Co.) was purified and collected by preparative glpc on a 20 in. × $^3/_8$ in. 20% SE-30 on Chromosorb W column. Iodobenzene dichloride (IBD) was prepared by the method of Lucas and Kennedy.[18] The IBD was recrystallized from chloroform and air dried before use.

The IBD prepared in this manner was (98–100%) pure by iodometric titration. Carbon tetrachloride (Fisher spectral grade) was used without further purification.

Nortricyclyl chloride (IV), *exo*-2-*syn*-7-dichloronorbornane (V), and *trans*-2,3-dichloronorbornane (II) were prepared by the method of Roberts, Johnson, and Carboni.[13] Infrared spectra of these compounds were identical with those reported by these workers. The *trans* isomer II had the nmr spectrum previously reported for this compound.[9]

Compounds IV and V showed nmr spectra which were consistent with these assigned structures: IV, τ 6.23, 7.5–9.0, with intensities of 1:8.7; V, τ 6.26 (multiplet), 7.3–9.0 (multiplet), with intensities of 2:8.3.

Diels-Alder Reaction of *cis*-Dichloroethene and Cyclopentadiene.—A mixture of dicyclopentadiene (90 g, 0.68 mole) and *cis*-dichloroethene (200 g, 2.0 moles) was sealed in three combustion tubes each containing hydroquinone (0.150 g). The mixtures were heated at 190° for 10 hr. The combined reactions were subjected to glpc analysis and showed, besides the starting *cis*-dichloroethene, two major products (>95%) in a 3:7 ratio. The reaction mixture was distilled through a 2.5-ft spinning-band distillation column at reduced pressures. The second fraction, bp 124–135° (41 mm), approximately 134 g, solidified in the receiver. This fraction was shown by glpc (10 ft × 0.25 in. SF-96 column) to contain a mixture of the major products in the same 3:7 ratio as seen in the crude reaction mixture. These two components were isolated by preparative glpc on the same column and their nmr spectra showed them to be the isomeric dichlorides VI and VIII, VI being the most abundant of the two dihalides. The nmr spectrum of VI was the same as that previously reported for the *cis,endo* isomer.[15] The infrared spectrum and

---

[17] R. G. Flowers and H. F. Miller, *J. Am. Chem. Soc.*, **69**, 1388 (1947).

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

melting point of VI was identical with those previously reported.[12]

The nmr spectrum of VIII showed contamination with VI and had absorption at τ 3.85, 6.10, 7.05 and 7.6–8.8. The glpc analysis showed that VIII was contaminated with 14% VI.

Anal. Calcd for $C_7H_8Cl_2$: C, 51.53; H, 4.91. Found: C, 51.67; H, 4.84.

The fraction from the distillation of the reaction mixture was recrystallized from cold pentane and 70 g of VI was isolated. The filtrate from this recrystallization shown by glpc analysis to be enriched in VIII was 65% VIII and 35% VI.

The enriched mixture was subjected to catalytic hydrogenation with PtO_2 according to the method used by Roberts.[13] This mixture yielded two isomeric dichlorides, IX and III, after the uptake of 1 mole of hydrogen. Analysis by nmr and glpc showed the mixture to be 65% III and 35% IX. The products were separated and collected by preparative glpc from a 20 ft × 0.25 in. SF-96 column. Compound IX had an identical mp 71–74° and infrared (CS_2) spectrum as those reported by Roberts.[13]

Compound III, a liquid, was shown by its nmr and microanalysis to be isomeric to IX and was assigned the structure of *exo,cis*-2,3-dichloronorbornane. The nmr spectrum of III was in agreement with that reported for this compound[8] and showed absorption at τ 6.06 (doublet, $J = 2$ cps), 7.55 (multiplet), and 7.7–8.9 (unresolved multiplet) with intensities of 2.0:2.0:6.0.

Anal. Calcd for $C_7H_{10}Cl_2$: C, 50.90; H, 6.06. Found: C, 51.02; H, 6.01.

Reactions of IBD and Norbornene.—Reactions were carried out in sealed Pyrex ampoules. Reactions which were run in the absence of molecular oxygen were degassed by the freeze–thaw method. The ampoules were continuously shaken during either the thermal or photoinitiated experiments. Photoinitiation was carried out using a Hanovia lamp (model 30620) or two 200-w incandescent light bulbs. The reaction was completed when the solid IBD had all gone into solution and the reaction mixture was clear. The reaction was shown to be complete by iodometric titration.

Typical reaction mixtures were 2–3 ml of 0.15–0.8 *M* norbornene in carbon tetrachloride and 0.13–0.23 mmole/ml of iodobenzene dichloride.

Analysis of Reaction Mixtures.—The product mixtures were analyzed by glpc on both a 10 ft × 0.25 in., 15% SF-96 on firebrick column and a 10 ft × 1/8 in., 5% SE-30 on Chromosorb W column or on a 30 ft × 1/8 in. column consisting of 20-ft 5% SE-30 and 10-ft 5% SE-96 on Chromosorb W. The chromatographic bands were identified by their comparison with the retention times of the authentic samples on the two columns. The products of typical reactions were collected from the SF-96 column and the nmr and infrared spectra were shown to be identical with those of the authentic compounds. Percentages were calculated for the integrated areas of the chromatographic peaks by the method of peak height times peak width at one-half peak height.

Material Balance.—The material balance for typical reactions was obtained, in the usual manner,[9] using Freon 112 as the internal standard. Molar ratios were calculated from calibration curves of Freon 112 and the authentic samples. In the case of the halogenated norbornanes the calibration curve for II was used as a typical curve for all of the halogenated norbornanes.

Registry No.—I, 498-66-8; III, 14627-75-9; IV, 3509-46-4; V, 4660-48-4; VIII, 14627-78-2; *cis*-dichloroethenes, 156-59-2; cyclopentadiene, 542-92-7.

Acknowledgment.—The authors wish to thank the National Research Council of Canada and the University of Alberta for their generous support of this work.

Intramolecular Alkylation as an Approach to Cyclic Sulfones and Sulfides

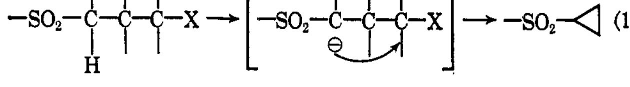
W. E. TRUCE, K. R. HOLLISTER, L. B. LINDY, AND J. E. PARR

Department of Chemistry, Purdue University, Lafayette, Indiana

Received August 10, 1967

A variety of cyclobutyl, cyclopentyl, and substituted pentamethylene sulfones have been prepared by α,ω-dehydrohalogenation of the corresponding ω-chloroalkyl sulfones. Several aryl cyclopropyl sulfides and 2-phenyltetrahydrothiophenes have also been prepared in this manner from the ω-chloroalkyl sulfides. This approach represents a useful synthesis of these and similar types of compounds.

A previous communication from this laboratory[1] described the preparation of cyclopropyl sufones by α,γ-dehydrohalogenation of various γ-chloropropyl sulfones (eq 1). This approach to cycloalkyl sulfones



$$-SO_2-\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-X \longrightarrow \left[-SO_2-\underset{\ominus}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\overset{|}{C}-X\right] \longrightarrow -SO_2-\triangleleft \qquad (1)$$

has been extended in the present communication to include the preparation of cyclobutyl and cyclopentyl sulfones and cyclopropyl sulfides. Furthermore, the dehydrohalogenation procedure gives rise to substituted pentamethylene sulfones or 2-phenyltetrahydrothiophenes when permitted by the structures of the precursors.

Cyclobutyl sulfones had not previously been investigated except for the probable preparation of methyl cyclobutyl sulfone,[2] in low yield, from reaction of cyclobutyl bromide with sodium methanesulfinate. The cyclopentyl sulfones, however, have commonly been prepared by oxidizing the corresponding sulfides, by treating cyclopentyl halides with sodium sulfinates, or by treating cyclopentanesulfinates with alkyl halides.[2–7] Variously substituted pentamethylene sulfones are known, prepared by oxidation of the corresponding sulfides.[8]

Cyclopropyl sulfides have been known since 1962, prepared in each case by reaction of chloromethyl sulfides with olefins in the presence of potassium *t*-butoxide, presumably through a carbene intermediate.[9–11] α-Substituted tetrahydrothiophenes have been pre-

---

[1] W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961).

[2] W. E. Truce and J. P. Milionis, *ibid.*, **17**, 1529 (1952).

[3] S. Archer, C. M. Suter, and B. F. Tullar, British Patent 668,562 (March 19, 1952); *Chem. Abstr.*, **47**, 5447 (1953); also U. S. Patent 2,618,640 (Nov 25, 1952).

[4] F. G. Bordwell and R. J. Kern, *J. Am. Chem. Soc.*, **77**, 1141 (1955).

[5] J. Weinstock, R. G. Pearson, and F. G. Bordwell, *ibid.*, **78**, 3473 (1956).

[6] H. L. Goering, D. I. Relyea, and I. I. Howe, *ibid.*, **79**, 2502 (1957).

[7] E. G. Perevalova, O. A. Nesmeyanova, and I. G. Luk'yanova, *Dokl. Akad. Nauk SSSR*, **132**, 853 (1960); *Chem. Abstr.*, **54**, 21025 (1960).

[8] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1960, pp 94–95.

[9] U. Schollkopf, *et al.*, *Tetrahedron Letters*, 165 (1962); *Chem. Ber.*, **97**, 1527 (1964); *ibid.*, **99**, 806 (1966).

[10] H. Reimlinger, *Chem. Ind.* (London), 1682 (1966).

[11] A. M. van Leusen, R. J. Mulder, and J. Strating, *Rec. Trav. Chim.*, **86**, 225 (1967).