The Reaction of Propene with Iodine Bromide

Vincent Alberts^A and Raymond M. Carman^{A,B}

^A Chemistry Department, University of Queensland, St. Lucia, Qld. 4067. ^B Author to whom correspondence should be addressed.

Abstract

Iodobromination of propene gives a mixture (c. 60: 40) of 2-bromo-1-iodopropane and 1-bromo-2-iodopropane. This mixture of kinetic control converts into an equilibrium (c. 70: 30) mixture with heat. The addition to the double bond is postulated to occur through a bridged iodonium ion rather than through a simple carbocation, and hence Markownikoff's rule need not apply to this system.

Introduction

A modern elementary textbook¹ deals with the problem of the addition of IBr to propene. The author suggests that the mechanism involves the Markownikoff* addition of I^+ (or its equivalent) to give the secondary carbocation (1) which with

* Markownikoff's rule, in its modern form, is expressed in a number of different ways. It seems that practising chemists use the term 'Markownikoff's rule' loosely in at least two ways: one to define a product, the other to define a mechanism. Brown¹ states the rule in a classical manner: 'the positive part of the reagent adds to the carbon that contains the greater number of hydrogen atoms' and then adds the modification that the reaction proceeds through the more easily formed carbocation. March² also states the rule in the classical way. Morrison and Boyd³ say that the product will be derived from the more stable carbonium ion, although they state that this more general rule replaces Markownikoff's original rule and they imply that this modern expression should not be called 'Markownikoff's rule'. Alder, Baker and Brown⁴ state that addition 'will be determined by the attack of nucleophile at the centre of highest carbonium ion stability, and that this is the basis of the classic Markownikoff rule'. Roberts and Caserio⁵ express the rule in its original form, and see the statement ' X^+ will be expected to add to the alkene to form the more stable carbocation' as 'an extension' of Markownikoff's rule. The latter authors also point out that one isomer is normally formed to the exclusion of the other in additions to unsymmetrical double bonds, because the energies of the various carbocations are primary \gg secondary \gg tertiary. Isenberg and Grdinic⁶ express the rule in classical form and then say the rule may be formulated: 'addition of X^+ will occur in such a manner as to give the more stable carbonium ion'. Clearly if this latter definition is used for Markownikoff's rule, the rule then need not apply, nor give guidance, to reactions which do not proceed through a simple carbocation, and one must be careful to define the meaning of 'anti-Markownikoff addition' where carbocations may not be involved as intermediates.

¹ Brown, W. H., 'Introduction to Organic Chemistry' 2nd Edn, p. 76 (Willard Grant: Boston 1978); Brown, W. H., 'Study Guide to Accompany Introduction to Organic Chemistry' 2nd Edn, p. 30 (Willard Grant: Boston 1978).

² March, J., 'Advanced Organic Chemistry' 2nd Edn, p. 687 (McGraw-Hill: New York 1977). ³ Morrison, R. T., and Boyd, R. N., 'Organic Chemistry' 3rd Edn, p. 195 (Allyn & Bacon: Boston 1973).

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bromide ion then gives 2-bromo-1-iodopropane (2). This argument ignores the well known neighbouring group effects of the iodine atom together with the possibility of the bridged iodonium cation (3).^{7,8}

The ion (3) need not be completely symmetrical. Inductive effects suggest greater positive charge on the secondary carbon, but the primary carbon is less hindered to attack by bromide. Hence a mixture of (2) and isomer (4) might be predicted from reaction of propene with IBr.

Surprisingly, no mention of isomers (2) or (4) could be found in *Chemical Abstracts*, although a reference dating back to 1874 appears in Beilstein.⁹ We also found no reference to the isomer composition of products formed in 'iodine number' titrations of olefins. Consequently we have investigated the reaction of mixed halides with propene.



Discussion and Results

The ratios of products formed in the reaction of mixed halides with propene in carbon tetrachloride at 0° are listed in Table 1. These ratios were determined by ¹H n.m.r. and ¹³C n.m.r. spectroscopy and gas-liquid chromatography, with relevant n.m.r. assignments (Table 2) obtained with assistance from the spectra of the authentic 1,2-diiodo-, 1,2-dibromo- and 1,2-dichloro-propanes.

Appreciable amounts of both 2-bromo-1-iodopropane (2) and 1-bromo-2-iodopropane (4) were formed in the reaction between propene and IBr. The ratio (60:40) was not an equilibrium; this was attained from either direction at 95° and gave (2): (4) 70: 30. This equilibrium presumably occurs through the intermediate (3), and could also be attained from the original 60:40 mixture with excess of bromide ion under phase-transfer conditions.

⁴ Alder, R. W., Baker, R., and Brown, J. M., 'Mechanism in Organic Chemistry' p. 301 (Wiley-Interscience: London 1971).

⁵ Roberts, J. D., and Caserio, M. C., 'Basic Principles of Organic Chemistry' 2nd Edn, p. 373 (Benjamin: Menlo Park 1977).

⁶ Isenberg, N., and Grdinic, M., J. Chem. Educ., 1969, 46, 601.

⁷ Olah, G. A., 'Halonium Ions' p. 98 (Wiley-Interscience: New York 1975).

⁸ De la Mare, P. B. D., 'Electrophilic Halogenation' p. 159 (Cambridge University Press: Cambridge 1976).

⁹ 'Beilsteins Handbuch der Organischen Chemie' p. 115 (Julius Springer: Berlin 1918).

Short Communications

Diiodide (5) is in equilibrium with propene and iodine, and pure diiodide (5) in CCl_4 gave propene (c. 5%) after 24 h at room temperature. This equilibrium presumably also proceeds through intermediate (3). Diiodide (5) in CCl_4 with bromide ion under phase-transfer conditions gave complete conversion into bromo iodides (2) and (4) in a similar ratio (70:30) as that observed above, confirming that the same intermediate could be involved. Little or no dibromide (6) was formed in this reaction.

CH ₃ -CHX-CH ₂ Y	CH₃–CHY–CH₂X	CH ₃ -CHX-CH ₂ X	CH ₃ -CHY-CH ₂ Y	
31	47	12	9	
17	41	19	23	
15	32	37	16	
27	63	10	0	
35	55	5	5	
	CH ₃ -CHX-CH ₂ Y 31 17 15 27 35	$\begin{array}{ccc} CH_3-CHX-CH_2Y & CH_3-CHY-CH_2X \\ \hline 31 & 47 \\ 17 & 41 \\ 15 & 32 \\ 27 & 63 \\ 35 & 55 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	

Table 1.	Products from	the reaction (of propene	with halo	gen halides	(XY)
						· ·

^A See Experimental for three different syntheses of ICl.

Table 2.	¹ H and	¹³ C	n.m.r.	shift	data	(δ	from	SiMe ₄)	for	compounds
			CF	I₃–CI	HX-C	H_2	Y			

X	Y	CH ₃	CHX	CH ₂ Y	C3	C2	C1
I	I	2.01	4.38	3.63, 4.07	28.46	21.83	14.62
I	Br	$2 \cdot 02$	Α	A	26.32	21.64	39.09
Br	I	1.87	Α	Α	25.54	45.03	11.55
I	Cl	1.99	Α	Α	25.20	22.25	50.95
Cl	Ι	1.69	Α	Α	24.42	54.90	11.33
Br	Br	1.84	4.20	3.49, 3.86	23.93	44.84	36.87
Br	Cl	$1 \cdot 80$	Α	A	23.05	45.47	49.03
Cl	Br	1.65	А	· A	23.05	54.71	36.82
Cl	Cl	$1 \cdot 62$	4.05	3.48, 3.75	22.20	54.90	48.69

^A Spectra of unassigned protons were complex and/or overlapping.

The diiodide (5), or the mixture of bromo iodides (2) and (4), with chloride ion under phase-transfer conditions gave similar mixtures of chloro iodides (7) and (8) (c. 65:35). Solutions of diiodide (5) when decolorized with sodium thiosulfate rapidly regenerated the colour of free iodine. Solutions of (2) and (4), when treated similarly, develop colour much more slowly.

The above data are consistent with the formation of the iodonium cation (3) in the iodobromination of propene. This ion is then rapidly converted into both isomers (2) and (4), which equilibrate much more slowly to give a mixture in which isomer (2) predominates. Clearly Markownikoff's rule need not give guidance to product ratios in such a system. The participation of the bridged bromonium ion (9) in the bromo iodo system is discounted as no bromochloropropanes were obtained from (2) and (4) with chloride ion, and no dibromides were formed with bromide ion.

The reaction of bromine with either diiodide (5) or the bromo iodides (2) and (4) in carbon tetrachloride gave dibromide (6) rapidly and quantitatively. The reaction of chloro iodides (7) and (8) with bromine was much slower. After two weeks, the mixture comprised isomers (10), (11) and (6) in the ratio 10:85:5. Reaction of chloro iodides (7) and (8) with bromide ion under phase-transfer conditions proceeded

very slowly; this suggests that the iodonium ion (3) forms much more slowly from chloro iodides (7) and (8) than from diiodide (5) or from iodo bromides (2) and (4).

Experimental

Unless otherwise stated, all reactions were carried out and all spectra determined in CCl₄ solution. Gas chromatography (60° for diiodides, 80° otherwise; over SE 30 on Varian Chromosorb W in stainless steel columns) gave relative R_1 values of 0.38 (1,2-dichloropropane), 0.64 (mixture (10)+(11)), 1.00 (dibromide (6)), 1.2 (mixture (7)+(8)), 2.0 (mixture (2)+(4)), 4.3 (diiodide (5)). The diiodide decomposed at 80°.

Bromoiodopropanes (2) and (4)

Iodine bromide was prepared¹⁰ by mixing bromine $(16 \cdot 0 \text{ g})$ with iodine $(25 \cdot 4 \text{ g})$ at 0° and warming the mixture (45°, 30 min). Cooling gave solid iodine monobromide which was recrystallized twice from its own melt. Iodine bromide $(10 \cdot 0 \text{ g})$ suspended in CCl₄ (50 ml) was treated with propene gas (0°, 1 h). Excess propene was removed in a stream of nitrogen. The product ratios are listed in Table 1, with n.m.r. spectral data in Table 2. Decolorized (sodium thiosulfate) solutions slowly became coloured at room temperature, and after 24 h showed the presence of propene (5%). The ratio of isomer (2) to (4) (60 : 40) altered at 95° (Büchi evaporator, 2 h, 500 mm) to a ratio of 70 : 30. No changes at 50° were observed over a 2 h period.

Material enriched in isomer (2) was chromatographed over silica from pentane. Elution with pentane gave some separation ((2): (4) = 63:37 in the early fractions; 82:18 in later fractions). Oil containing (2) and (4) (82:18) at 95° (2 h) rearranged to give the 70: 30 mixture observed above.

Diiodopropane (5)

Propene was bubbled (3 h) into a stirred solution of iodine $(8 \cdot 5 \text{ g})$ in CCl₄ (100 ml). The pink solution was freed of excess propene with a stream of nitrogen at 15°; considerable darkening occurred. The solution regenerated propene (n.m.r.) on standing at 20°.

Chloroiodopropanes (7) and (8)

(a) Chlorine was passed through iodine $(12 \cdot 0 \text{ g})$ until the weight had increased by $3 \cdot 55 \text{ g}.^{11}$ Iodine $(0 \cdot 7 \text{ g})$ was added. The mixture was warmed and allowed to cool slowly. When 80% of the product had crystallized, the liquid was decanted.

The iodine chloride, suspended in CCl₄ at 0° , was treated with a propene stream for 3 h. Excess propene was removed with nitrogen.

(b) Chlorine $(8 \cdot 0 \text{ g})$ in CCl₄ (50 ml) was treated with iodine $(28 \cdot 7 \text{ g})$ and the mixture was stirred (20°, 2–3 days) following the method used to make bromine chloride.¹² Propene was then bubbled through the mixture, followed by nitrogen.

(c) Propene was bubbled through a mixture¹³ of cupric chloride $(13 \cdot 3 \text{ g})$ and iodine $(12 \cdot 7 \text{ g})$ in CCl₄ (50 ml). The mixture was filtered and the filtrate flushed with nitrogen gas.

Bromochloropropanes (10) and (11)

Chlorine $(3 \cdot 7 \text{ g})$ in CCl₄ (50 ml) with bromine¹² (8 \cdot 3 g) was cooled (0°) and treated with propene. A fast stream of nitrogen was used to remove excess propene.

Reaction of the Dihalopropanes with I_2 and Br_2

The dihalopropanes in CCl₄ were mixed with I_2 or Br_2 and stored in the dark at 20°. The reactions were followed by n.m.r. spectroscopy.

(a) Diiodopropane (5) with Br_2 gave 1,2-dibromopropane (100%) within 2 min.

¹⁰ 'Handbook of Preparative Inorganic Chemistry' (Ed. G. Brauer) Vol. 1, 2nd Edn, p. 291 (Academic Press: New York 1963).

¹¹ 'Inorganic Syntheses' (Ed. S. Y. Tyree, Jr) Vol. 9, p. 130 (McGraw-Hill: New York 1967).

¹² Findlay, M. C., Waters, W. L., and Caserio, M. C., J. Org. Chem., 1971, **36**, 275.

¹³ Baird, W. C., Surridge, J. H., and Buza, M., J. Org. Chem., 1971, 36, 2088.

(b) The bromoiodopropane mixture (2) and (4) with Br_2 gave 1,2-dibromopropane (100%) within 6 min.

(c) Treatment of a mixture of the chloroiodopropanes (7) and (8) with Br_2 gave a mixture of dibromide (5%) and bromochloropropanes (95%) after 2 weeks at 20°.

(d) The bromochloropropanes (10) and (11) with Br_2 were essentially unchanged after 1 week. (e) All the above mixed halides with I_2 showed starting dihalide (>95%) after 1 week.

Reaction of Dihalides with Bromide

(a) Diiodide (5) in CCl₄ (3 ml) was stirred with hexadecyl(trimethyl)ammonium bromide and saturated aqueous KBr (2 ml). After 2 weeks, the n.m.r. spectrum showed only bromo iodides (2) and (4) (60 : 40). After a further 2 weeks, the ratio had changed to 65 : 35.

(b) Bromo iodides (2) and (4) (60:40) under the same conditions for 2 weeks gave a changed ratio of 70:30.

(c) The chloro iodides (7) and (8) showed no reaction under these conditions.

Reaction of the Dihalides with Chloride ion

(a) The dihalide in CCl₄ (3 ml) was stirred with tetra-t-butylammonium chloride and saturated aqueous KCl (2 ml) at 20° .

(i) Diiodide (5) after 4 weeks gave iodo chlorides (7) and (8) (70 : 30). Shorter reaction time gave unchanged diiodide.

(ii) The iodo bromide mixture (2) and (4) after 3 weeks showed starting material (70%) plus iodo chlorides (30%) in the ratio (2): (4): (7): (8) = 52: 18: 17: 13.

(iii) Other dihalides did not react.

(b) The dihalide in CCl₄ (3 ml) was stirred with Amberlyst A-26 (chloride form) at 20° .

(i) Diiodide (5) after 3 days showed chloro iodides (7) and (8) with propene (50: 30: 20). The ratio of (7): (8) increased to 75: 25 after 3 weeks.

(ii) A mixture of bromo iodides (2) and (4) after 3 weeks showed starting material and chloro iodides in the ratio (2): (4): (7): (8) = 25: 15: 45: 15.

In these reactions, no bromochloropropanes were observed as products.

Acknowledgments

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