Tetrahedron Letters,Vol.26,No.12,pp 1399-1402,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

ON THE MECHANISM OF LIQUID PHASE HALOGENATION OF ADAMANTANE DERIVATIVES

A.G.Yurchenko, N.I.Kulik

Department of Chemical Technology, Polytechnic Institute, Kiev, 252056, USSR

V.P.Kuchar, V.M.Djakovskaja, V.F.Baklan

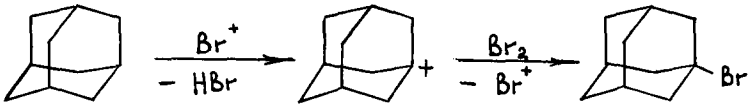
Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 252660, USSR

SUMMARY: The novel mechanistic representation of adamantane derivatives halogenation process is introduced.

Halogenation of alkanes and cycloalkanes in vapor or condensed phase is generally considered as a typical case of free radical substitution initiated thermally or photochemically [1]. In the last years a number of examples became available on the bromination with liquid bromine both cage (adamantane [2,3,4], protoadamantane [5], diamantane [6], 2,4-ethanoadamantane [7]) and alycyclic (decaline [8]) or even acyclic (triptane [9]) hydrocarbons. All these cases do not fit the free radical substitution mechanism because the bromination is not initiated by heat, light or radical sources, but is accelerated by Lewis acids.

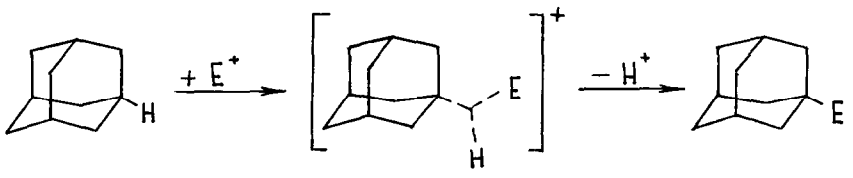
On this ground using only the results of preparative experiments Stetter[10] supposed the ionic bromination of adamantane (Scheme 1):

Scheme 1



Olah has studied the bromination [11] and chlorination [12] of adamantane with molecular bromine or chlorine in CH_2Cl_2 in the presence of Lewis acids. By analogy with alkane and cycloalkane protolysis mechanism [13] the author postulated the reaction to proceed as an electrophilic substitution with presupposed proton splitting out from the two electron three center transition state and the electrophyle entering into the reaction product (Scheme 2).

Scheme 2



Elementary steps sequence in Scheme 2 resembles that of electrophylic substitu-

tion in aromatic ring. The principal difference of Scheme 1 from 2 consists in assertion that nucleophilic part of the reagent enters into the reaction product though in the case of symmetrical reagents such as Br_2 or Cl_2 this difference is experimentally indistinguishable. Application of interhalogens as halogenating agents with clear determination of electrophylic and nucleophilic parts would help to make a choice between Schemes 1 and 2.

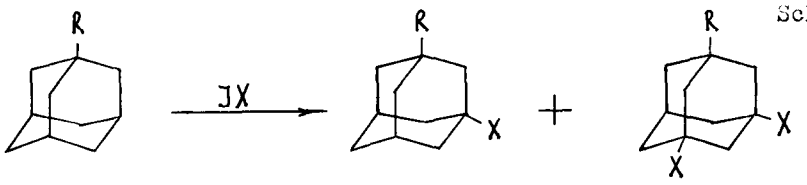
To check the validity of this assumption we have studied the halogenation of adamantane in CCl_4 solution with interhalogens - JBr and JCl in which the electrophylic part of the molecule is iodine atom. Depending on the halogenating agent excess, reaction time and temperature substitution of one or two bridgehead hydrogens for chlorine or bromine has been found. Neither iododerivatives nor 2-substituted adamantanes were detected by GLC in all experiments even in trace quantities [14]. Table 1 and Scheme 3 demonstrates the results of adamantane (1), 1-methyladamantane (2) and 1-adamantane carboxylic acid (3) halogenation [15].

Table 1

1-R- Ad, g	J-X, g	CCl_4, ml	Time, hrs	Temp.	Yield, %	
					1-R-3-X- Ad	1-R-3,5-X_2-Ad
	R = H,		X = Br			
1.0	20	15	3	reflux	75[a]	25[a]
	R = H,		X = Cl			
0.1	2.4	5	18	room	60[a]	40[a]
2.5	62	160	0.25	room	97[b]	-
1.0	60	80	5	reflux	-	98[b]
	R = CH_3,		X = Cl			
3.0	53.6	160	2	room	94[b]	-
3.3	180	285	5	reflux	-	84[b]
	R = COOH,		X = Cl			
3.2	58.7	160	5	reflux	83[b]	-

[a] GLC analysis: 5 % SE-30 on Chromaton N-AW-DMCS, 3 m x 3 mm, 170°C, helium as a carrier gas.

[b] Preparative yield of GLC pure substance.



Scheme 3

(1) R = H (4) R = H, X = Br (8) R = H, X = Br

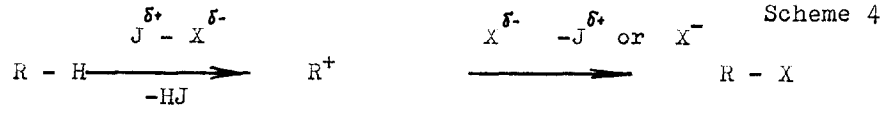
(2) R = CH_3 (5) R = H, X = Cl (9) R = H, X = Cl

(3) R = COOH (6) R = CH_3, X = Cl (10) R = CH_3, X = Cl

(7) R = COOH, X = Cl

In accordance with Scheme 2 adamantane iododerivatives formation should be expected. The resulting compounds observed in our experiments could be the consequence a) of direct substitution of bridgehead hydrogens in adamantane for substituent X in accordance with Scheme 1, being the primary substitution products or b) of exchange of iodine atoms in compounds formed in accordance with Scheme 2 for substituent X under the treatment with excess reagent JX. In the latter case the formation of disubstituted adamantanes should proceed as sequential substitution and exchange reactions.

We have found the 1-iodoadamantane readily to exchange iodine for chlorine or bromine under treatment with JCl or JBr [16] correspondingly, but 1,3-diiodoadamantane does not react with JCl or JBr under halogenation reaction conditions. The rate of exchange of iodine in 1-chloro-3-iodoadamantane should be even lower than in 1,3-diiodoadamantane, therefore all compounds formed in the halogenation of adamantane and its derivatives with interhalogens are primary reaction products and it is nucleophilic part of the reagent what enter the final reaction products. This can be depicted with quite a simplified Scheme 4:



Scheme 4

The results of the present study show the electrophyle in ionic halogenation reaction fulfil a heterolysis of the C-H bond but not enter the molecule of final product. Formally this reaction should be classified as nucleophilic substitution at saturated carbon atom with strong electrophylic assistance to heterolysis of C-H bond and hydride ion as a leaving group. The numerous cases of hydride mobility in ionic reactions of adamantane and its derivatives [17] may serve as a support of this assumption.

REFERENCES AND FOOTNOTES

(1) Comprehensive organic chemistry, vol.1, D.Barton, W.D.Ollis, editors,

Pergamon Press, N.Y., 1979.
(2) H.Stetter, M. Schwarz, A.Hirschhorn, Ber., 92, 1629 (1959).
(3) G.L.Baughman, J. Org. Chem., 29, 238 (1964).
(4) H.Stetter, C.Wulf, Ber., 93, 1366 (1960).
(5) A.Karim, M.A.McKervey, E.M.Engler, P.R.Schleyer, Tetrahedron Letters, 1971, 3987.
(6) T.M.Gund, P.R.Schleyer, G.D.Unruch, G.J.Gleicher, J. Org. Chem., 39, 2995 (1974).
(7) E.Osawa, E.M.Engler, S.A.Godlesky, Y.Inamoto, G.J.Kent, M.Kausch, P.R.Schleyer, J. Org. Chem., 45, 984 (1980).
(8) H.Stetter, E.Tresper, Ber., 104, 71 (1971).
(9) V.F.Baklan, R.K.Orlova, A.G.Yurchenko, Ukrainian Chemical Journal (USSR), 50, 760 (1984).
(10) H.Stetter, C.Wulff, Angew. Chem., 72, 351 (1960).
(11) G.A.Olah, P.Schilling, J. Am. Chem. Soc.,95, 7680 (1973).
(12) G.A.Olah, R.Renner, P.Schilling, Y.K.Mo, J. Am. Chem. Soc., 95, 7686 (1973).
(13) G.A.Olah, R.H.Schlosberg, J. Am. Chem. Soc., 90, 2726 (1968); G.A.Olah, Y.Halpern, J.Shen, Y.K.Mo, J. Am. Chem. Soc., 93, 1251 (1971).
(14) A.G.Yurchenko, V.M.Djakovskaja, V.F.Baklan, Zhur. Org. Chem., USSR, 20, 2239 (1984).
(15) Identification of the compounds (4)-(10) was made by IR, NMR and GLC comparison with authentic samples.
(16) R.M.Keefer, L.J.Andrews, J. Am. Chem. Soc., 75, 543 (1953).
(17) R.C.Fort, Adamantane, Marcel Dekker, Inc., N.-Y., 1976.

(Received in UK 8 January 1986)