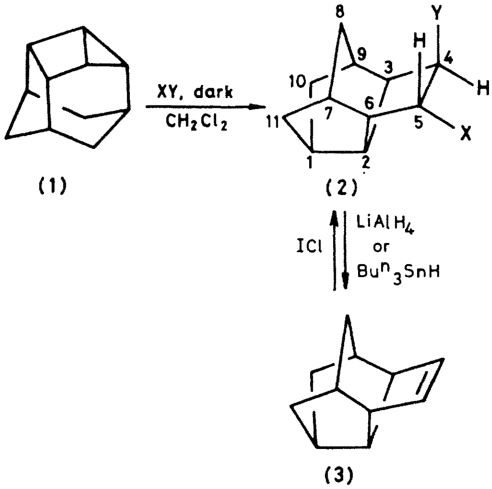
Front Side Attack[†] on the Bicyclo[2.1.0]pentane System by Halonium Ion; Halogenation of Dehydronoriceane[‡]

By TAKEO KATSUSHIMA, RYOHEI YAMAGUCHI, SATOSHI IEMURA, and MITUYOSI KAWANISI
(*Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto* 606, *Japan*)

Summary Halogenation of dehydronoriceane (**1**) in dichloromethane in the dark exclusively or predominantly gave the *trans*-4,5-dihalogenoethanonoradamantanes (**2**) providing decisive evidence for front side attack on the bicyclo[2.1.0]pentane system by halonium ions; the reaction is susceptible to the solvent and halogen used.

ALTHOUGH LaLond reported[1] that the halogenation of bicyclo[2.1.0]pentane gave predominantly *trans*-1,2-dihalogenocyclopentane and postulated that 1,2-hydride migration accompanied the formation of 1,2-halonium ions, mechanistic details including the stereochemical fate of the halogen (*e.g.*, whether front side attack[†] with retention of configuration or corner side attack with inversion of configuration occurs) remain unexplored. We have recently reported the synthesis of dehydronoriceane[‡] (**1**),[2] in which the bicyclo[2.1.0]pentane system is incorporated, and present here our preliminary results on the mechanistic aspects of the halogenation reaction of the bicyclo[2.1.0]pentane system as well as its susceptibility to the solvent and halogen used.

When dehydronoriceane (**1**) was treated with bromine in dichloromethane in the dark, only *trans*-4,5-dibromoethanonoradamantane (**2a**)[§] was obtained in 80% isolated yield.



(1)

(2)

(3)

a; X = Y = Br
b; X = Y = I
c; X = I, Y = Cl
d; X = H, Y = Cl

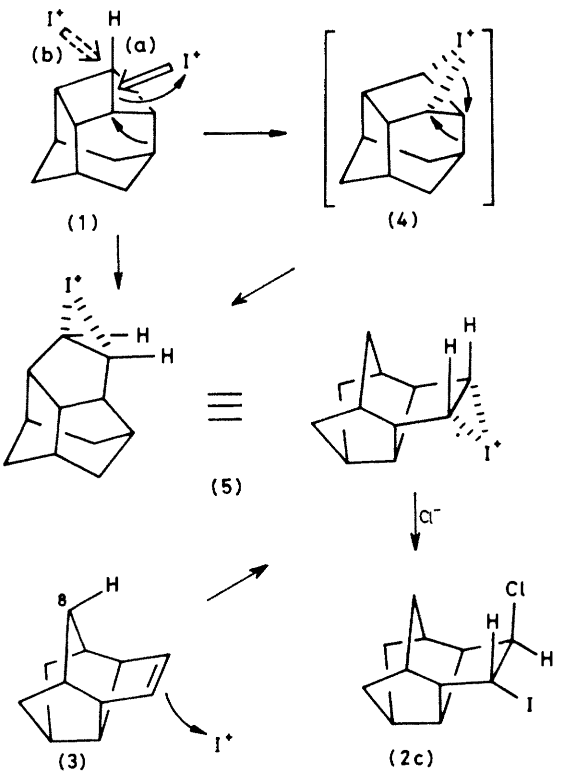
SCHEME 1

[†] Front side attack means that the halonium ion participates with the front lobe of the central bond of the bicyclo[2.1.0]pentane system and the initial attack proceeds with retention of configuration. Corner side attack means that the halonium ion participates with the back lobe and the attack proceeds with inversion of configuration.

[‡] I.U.P.A.C. name for dehydronoriceane; pentacyclo[5.3.1.$0^{2,6}$.$0^{3,5}$.$0^{4,9}$]undecane.

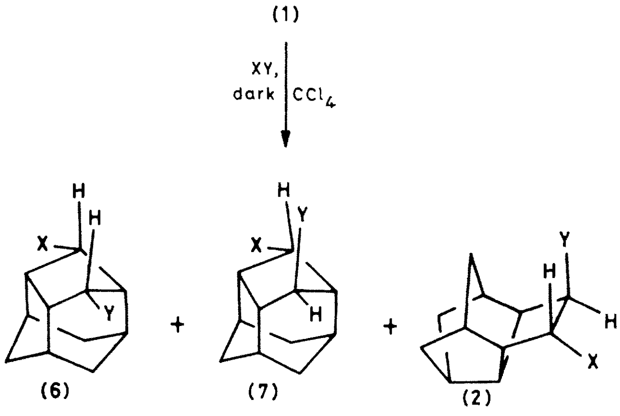
[§] I.U.P.A.C. name for ethanonoradamantane; tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane.

No other product could be detected by g.l.c. or ^{1}H-n.m.r. spectroscopy. The structure of (**2a**) was confirmed by elemental analysis, spectroscopic (^{1}H- and ^{13}C-n.m.r.) data, and the chemical transformation to ethenonoradamantane (**3**)[3] [(**2a**) m.p. 58—61 °C; ^{1}H-n.m.r. data $\delta(CCl_4)$ 4·70 (1H, dd, *J* 6·5 and 4·5 Hz), 4·47 (1H, d, *J* 4·5 Hz), 2·97 (1H, q, *J* 6·0 Hz), 2·82—2·42 (3H, br. complex m), 2·37—1·20 (8H, br. complex m); ^{13}C-n.m.r. data $\delta(CDCl_3)$ 61·5 (2CH), 58·0 (CH), 57·8 (CH), 47·3 (CH), 42·2 ($2CH_2$), 41·0 (CH), 39·4 (2CH), 30·1 p.p.m. (CH_2)]. Similar treatment of (**1**) with iodine gave predominantly *trans*-4,5-di-iodoethanonoradamantane (**2b**, 73%) along with the olefin (**3**, 12%) and the 1,3-di-iodides (**6b** and **7b**, *vide infra*, 14%), as shown by ^{1}H-n.m.r. spectroscopy. In order to investigate the stereochemistry of these halogenations, the reaction of (**1**) was effected with iodine chloride, the attacking species of which is the iodonium ion, under similar conditions to give only *endo*-4-chloro-*exo*-5-iodoethanonoradamantane (**2c**) in 78% isolated yield. The configurations of halogens in (**2c**) were determined as follows. (i) As the coupling patterns of 4-H and 5-H in the ^{1}H-n.m.r. spectrum resemble those of (**2a**) and (**2b**), the stereochemistry of the halogens should be *trans*. (ii) The selective reduction of (**2c**) with $Bu^{n}_{3}SnH$ gave 4-chloroethanonoradamantane (**2d**), the configuration of which was determined to be *endo* by comparison of its ^{1}H-n.m.r. spectrum with those of *exo*- and *endo*-4-hydroxyethanonoradamantanes.[4] (iii) The reaction of the olefin (**3**) with iodine chloride afforded the same chloroiodide (**2c**).



Scheme 2

Scheme 2 can best explain the above results. The initial attack on the bicyclo[2.1.0]pentane group by iodonium (or bromonium) ion must take place from the front side (a) with retention of configuration, but not from the corner side (b) with inversion of configuration. The subsequent C–C bond migration produces the 1,2-iodonium (or bromonium) ion (**5**) directly or through the 1,3-iodonium (or bromonium) ion (**4**). A nucleophile (*e.g.* Cl^-) captures (**5**) to afford the *trans*-dihalides (**2**). The same 1,2-iodonium ion (**5**) is also generated from the olefin (**3**) because of the steric hindrance due to 8-H. Thus, it has been established that halonium ions may participate with the central bond of the bicyclo[2.1.0]pentane system in an edge fashion and we believe that this is the first decisive experimental evidence for front side attack on the bicyclo[2.1.0]pentane system by halonium ions.



Scheme 3

Reagent XY	% Yield	Product ratio[a] (**6**):(**7**):(**2**)
a; X = Y = Br	77	1:33:52[b]
b; X = Y = I	59	42:58:0
c; X = I, Y = Cl	65	0:0:100

[a] Determined by g.l.c. and/or ^{1}H n.m.r. spectroscopy. [b] An unidentified product (14%) was also obtained.

Whereas the halogenation of (**1**) in dichloromethane takes place in ionic fashion to induce the skeletal rearrangement, we have found that the reaction in carbon tetrachloride is susceptible to the ionic nature of the halogen used. Thus, it is noteworthy that the 1,3-di-iodides (**6b**) and (**7b**), (59% isolated yield) were the only detectable products in the reaction of (**1**) with iodine in carbon tetrachloride in the dark. The structures of (**6b**) and (**7b**) were determined by elemental analysis, spectroscopic (^{1}H and ^{13}C n.m.r.) data, and the chemical transformation to (**1**).¶ Similar treatment of (**1**) with bromine gave the 1,3-dibromides (**6a**) and (**7a**) in addition to the *trans*-dibromide (**2a**) (77% isolated yield). Furthermore, it is interesting that in the case of iodine chloride only the *trans*-chloroiodide (**2c**) was detected. While mechanistic details for the

---

¶ The reduction of these 1,3-dihalides with lithium aluminium hydride regenerated the starting material (**1**).

formation of 1,3-dihalides are not clear yet,** we may conclude that the halogenation of the bicyclo[2.1.0]pentane system is sensitive to solvent polarity and the ionic nature of the halogen.[5]

(*Received*, 15*th October* 1979; *Com.* 1096.)

** A free radical type reaction might contribute to the formation of 1,3-dihalides, because halogenations of (**1**) under irradiation gave exclusively the 1,3-dihalides (**6**) and (**7**) in *ca.* 1 : 1 ratios.

[1] R. T. LaLond, *J. Amer. Chem. Soc.*, 1965, **87**, 4217.
[2] T. Katsushima, R. Yamaguchi, and M. Kawanisi, *J.C.S. Chem. Comm.*, 1975, 692.
[3] T. Katsushima, R. Yamaguchi, M. Kawanisi, and E. Ōsawa, *J.C.S. Chem. Comm.*, 1976, 39.
[4] T. Katsushima, R. Yamaguchi, and M. Kawanisi, unpublished results.
[5] It should be noted that in the case of the bicyclo[1.1.0]butane system 1,3-dihalogenocyclobutanes are the predominant products; K. B. Weiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 1965, **21**, 2749; S. Masamune, *Tetrahedron Letters*, 1965, 949; S. Mazur, A. H. Schroder, and M. C. Weiss, *J.C.S. Chem. Comm.*, 1977, 262.