Halogenation of 3,5-Dehydronoriceane (Pentacyclo[5.3.1.$0^{2,6}$.$0^{3,5}$.$0^{4,9}$]undecane.[1] Front Side Attack on the Bicyclo[2.1.0]pentane System by Halonium Ion and Corner Side Attack by Halogen Radical[2]

Takeo KATSUSHIMA, Ryohei YAMAGUCHI, Satoshi IEMURA, and Mituyosi KAWANISI*

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

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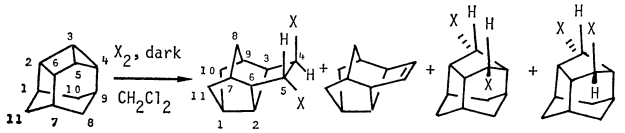
Halogenations of 3,5-dehydronoriceane (**1**) in dichloromethane in the dark exclusively or predominantly give *endo,exo*-4,5-dihalotetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecanes; these results provide a decisive evidence for the front side attack on the bicyclo[2.1.0]pentane system by halonium ion. On the other hand, the corner side attack on the bicyclo[2.1.0]pentane system by halogen radicals takes place in photohalogenations of **1**, which give *endo,endo*- and *endo,exo*-3,5-dihalonoriceanes. In addition, the halogenation of **1** in the dark is found to be sensitive to the solvent polarity and the ionic nature of the halogen used. Bromination of **1** in nonpolar solvents in the dark likely proceeds through intervention of the 1,3-bridged bromonium ion.

In 1965 LaLond[3] reported that halogenation of bicyclo[2.1.0]pentane gave predominantly *trans*-1,2-dihalocyclopentane. On the basis of the results, he postulated the mechanism that consisted of conversion of an initially formed 1,3-bridged halonium ion into 1,2-bridged one *via* 1,2-hydride migration. To our knowledge, there has been no further report on the mechanism of halogenation of bicyclo[2.1.0]pentane system. Either the validity of the above mechanism or mechanistic details including the stereochemical fate of the halogen (*i.e.*, whether front side attack with retention of configuration or corner side attack with inversion of configuration) remains unexplored.[4] We have recently reported the synthesis of 3,5-dehydronoriceane (**1**)[5] and expect that **1** is a likely model compound for solving the above problems to some extent, because **1** has the partial bicyclo[2.1.0]pentane structure constrained within a rigid cage structure. We now wish to desribe here our results on the stereochemical aspects of the halogenation reaction of bicylo-[2.1.0]pentane system as well as the susceptibility of the reaction to the solvent and the halogen used.[6]

Results and Discussion

*Halogenation of **1** in the Dark.* When **1** was treated with bromine in dichloromethane at −78 °C in the dark, *endo,exo*-4,5-dibromotetracylo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**2a**) was obtained predominantly along with a small amount of *endo,exo*-3,5-dibromonoriceane (**8a**) (*vide infra*) and an unidentified compound (**2a**:**8a**=90:5).[7,8] The structure of **2a** was determined by elemental analysis, spectroscopic data ^{1}H-NMR (PMR) and ^{13}C-NMR (CMR) which showed a lack of a plane of symmetry, and the debromination to tetracyclo-

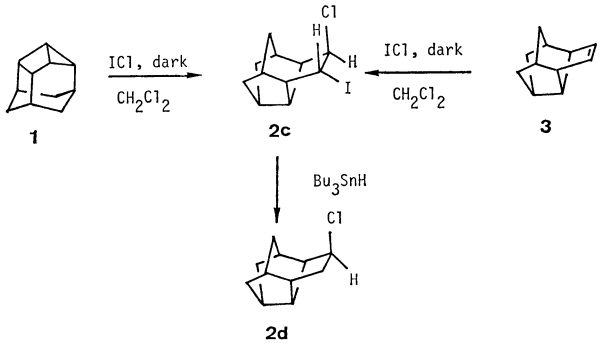


	1	2		3		7		8
a	X = Br	90	:	0	:	0	:	5
b	X = I	73	:	12	:	4	:	11

2a or 2b —LAH→ 3

Scheme 1.

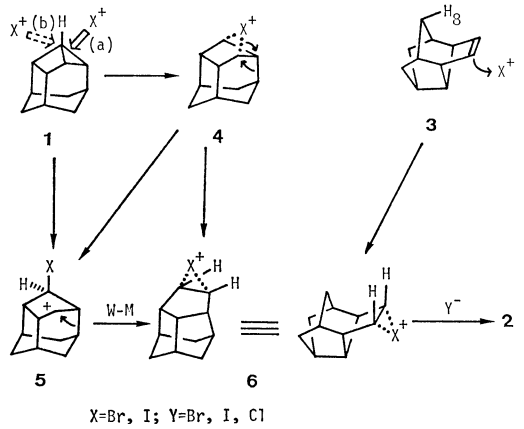
[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene (**3**)[9] with lithium aluminium hydride. A similar treatment of **1** with iodine gave predominantly *endo,exo*-4,5-diiodotetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane(**2b**), along with **3** and *endo,endo*- and *endo,exo*-3,5-diiodonoriceanes (**7b** and **8b**, *vide infra*) (**2b**:**3**:**7b**:**8b**=73:12:4:11). Although **2b** has never been isolated in a pure form because of its rapid decomposition to the olefin (**3**), the structure of **2b** has been elucidated by a resemblance between the PMR spectra of **2a** and **2b** as well as the chemical trans-formation to **3**.



Scheme 2.

In order to investigate the stereochemistry of these halogenations, the reaction of **1** was effected with iodine chloride, the attacking species of which was the iodonium ion, under a similar conditions to the above. This gave exclusively *endo*-4-chloro-*exo*-5-iodotetracyclo-[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**2c**) in 78% yield. The configurations of halogens in **2c** were determined as follows. (i) As the coupling patterns of H_4 and H_5 in the PMR spectrum resemble those of **2a** and **2b**, the stereochemistry of the halogens should be trans. (ii) The selective reduction **2c** with Bu_3SnH gave 4-chlorotetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**2d**), the PMR spectrum of which showed a quintet at 4.55 ppm due to H_4. Since PMR spectra of *exo*- and *endo*-4-tetracyclo-[5.3.1.$0^{2,6}$.$0^{3,9}$]undecanols have shown a doublet of doublet at 4.33 ppm and a quintet at 4.58 ppm, respectively, due to H_4,[10] the configuration of the chlorine substituent in **2d** is determined to be *endo*. (iii) Furthermore, the reaction of **3** with iodine chloride afforded the same chloro iodo compound (**2c**).

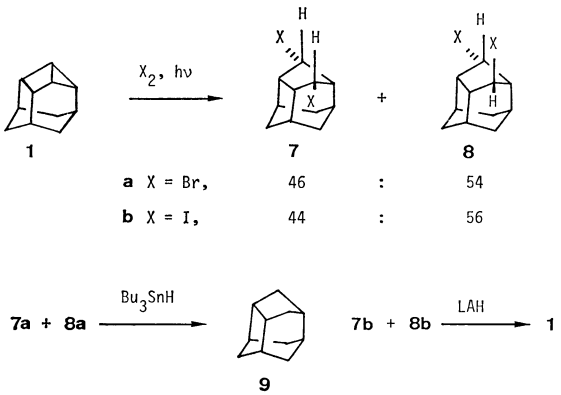
Scheme 3 can best explain the above results. The



Scheme 3.

initial attack on the bicyclo[2.1.0]pentane group by halonium ion (X^+) must take place from the front side (a) with retention of configuration, but not from the corner side (b) with inversion of configuration. The resulting carbocation intermediate (**5**) may undergo Wagner-Meerwein (W-M) rearrangement to give an 1,2-bridged halonium ion (**6**). It would be also possible that **6** is produced through an 1,3-bridged halonium ion (**4**), as is shown in Scheme 3. A nucleophile (Y^-) captures **6** to afford the *trans*-dihalides (**2**). The same 1,2-bridged halonium ion (**6**, X=I) is also generated from the olefin (**3**) because of the steric hindrance due to H_8. 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.

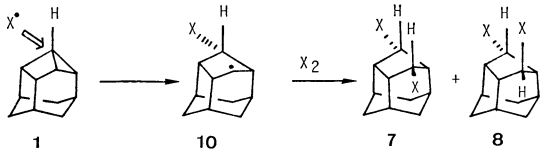
Photohalogenation of ***1***. While halogenations of **1** in dichloromethane in the dark give predominantly or exclusively the rearranged products (**2**), a small amount of unrearranged 1,3-addition products (**7** and **8**) is also produced, especially in the iodination. We, therefore, have investigated photohalogenations of **1**, because it has been known that photohalogenations of cyclopropanes take place in a radical fashion to give 1,3-dihalides.[11] When **1** was allowed to react with bromine in carbon tetrachloride under the irradiation through soft glass filter by means of 300 W medium-pressure mercury arc, *endo,endo*- and *endo,exo*-3,5-dibromonoriceanes (**7a** and **8a**) were obtained in 72% combined yield (**7a**:**8a**=46:54). Similarly, a photoiodination of **1** under the daylight[12] gave *endo,endo*- and *endo,exo*-3,5-diiodonoriceans (**7b** and **8b**) in 96% combined yield (**7b**:**8b**=44:56).



Scheme 4.

The structures of **7** and **8** were determined as follows. Reduction of the mixture of **7a** and **8a** with Bu_3SnH gave noriceane (**9**)[5] and deiodination of **7b** and **8b** with lithium aluminium hydride reproduced **1**. Since **8a** and **8b** have been shown to have to symmetry by NMR analyses, these must be *endo,exo*-3,5-dihalonoriceanes. The PMR spectra of **7a** and **7b** showed only one kind of a broad singlet with half-width of 8.5 Hz due to H_3 and H_5. In noriceane system, the *exo*-H_3 (or H_5) appears as a broad singlet with half-width of *ca.* 8.5 Hz and *endo*-one does as a sharp singlet with half-width of *ca.* 3 Hz.[13] Consequently, **7a** and **7b** were determined to be *endo,endo*-3,5-dihalonoriceanes.

Thus, it has been found that photohalogenations of **1** give *endo,endo*- and *endo,exo*-3,5-dihalonoriceanes in a ratio of *ca.* 1:1. No *exo,exo*-isomer has been detected. These results are compatible with the mechanism which has been suggested for photohalogenations of cyclopropanes.[11] According to the mechanism, the initial attack on the bicyclo[2.1.0]pentane system by halogen radical takes place from the corner side with inversion of configuration to give *endo*-3-halonoricyl radical (**10**). The subsequent non-stereoselective abstraction of a halogen atom from a halogen molecule can give a mixture of an almost equal amount of **7** and **8** (Scheme 5).



Scheme 5.

Solvent Effects on the Halogenation of ***1***. In addition to the new insight mentioned above on the halogenation of **1**, we have found that considerable amount of the unrearranged dihalides (**7** and **8**) are produced even in the dark when the solvent is changed from dichloromethane to carbon tetrachloride (Table 1). As shown in Table 1, the iodination did not give the rearranged product (**2b**) but the unrearranged ones (**7b** and **8b**). In the case of the bromination, both of the rearranged and unrearranged dibromides were formed. Furthermore, it is interest-

Table 1. Halogenation of **1** in CCl_4 in the dark

	Halogens	Yield/%	Products ratio/%[a] 2 : 7 : 8
a	X=Y=Br	77	52 : 1 : 33[b]
b	X=Y=I	59	0 : 42 : 58
c	X=I, Y=Cl	95	100 : 0 : 0

a) Determined by GLC and/or PMR analyses.
b) An identified product was also obtained.

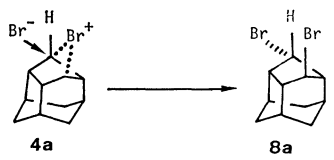
TABLE 2. BROMINATION OF **1** IN VARIOUS SOLVENTS IN THE DARK

Run	Solvent	E_T-value[a]	Temp/°C	Products ratio/%[b,c]			
				2a :	**7a** :	**8a**	**7a/8a**
1	CH_2Cl_2	41.1	−78	91	0	5	0
2			15[d]	90	0	5	0
3	$CHCl_3$	39.1	−78	89	0	6	0
4			15[d]	80	0	12	0
5			61[e]	74	0	22	0
6	Et_2O	34.6	−78	19	30	37	0.81[f]
7			15[d]	51	12	26	0.46[f]
8	CCl_4	32.5	−23[g]	85	0	10	0
9			15[d]	52	1	33	0.03
10	Cyclohexane	31.2	6[g]	39	14	41	0.34
11			15[d]	51	11	32	0.34

a) Taken from Ref. 14. b) Determined by GLC analysis. c) In all cases except for ether, a small amount of an unidentified product was formed.[8] d) Room temperature. e) Reflux temperature. f) Two unidentified products were formed. g) Freezing point of the solvents.

ing that the iodochlorination gave only the rearranged product (**2c**). These results strongly suggest that the iodination of **1** in carbon tetrachloride proceeds in a radical fashion even in the dark and that the iodochlorination takes place in an ionic fashion regardless of the polarity of the solvent. In addition, attention should be paid to the predominant formation of the *endo,exo*-isomer (**8a**) over the *endo,endo*-one (**7a**) in the bromination; this indicates the possibility of another non-radical reaction pathway. We, therefore, have investigated the solvent effects on bromination of **1** in more detail.

Table 2 summarizes the results. Two major distinctive features should be mentioned as follows. (i) As the polarity (E_T-value)[14] of the solvent decreases, the formation of the unrearranged products (**7a** and **8a**) increases. (ii) More *endo,exo*-isomer (**8a**) is always formed than the *endo,endo*-one (**7a**). Especially in runs of 1—5, 8, and 9, **8a** is exclusively produced over **7a**. This is in a marked contrast to the bromination of bicyclo[3.1.0]hexane in chloroform in the dark which gives *cis*- and *trans*-1,3-dibromocyclohexane in an almost 1:1 ratio.[4] The predominant or exclusive formation of the *endo,exo*-isomer (**8a**) can be best rationalized by assuming that a 1,3-bridged bromonium ion such as **4** (X=Br) mentioned before is captured by bromide ion (Scheme 6). It is highly probable that a lifetime of **4a** is longer in nonpolar solvents than in polar ones becasue the latters can stabilize a carbocation character by solvation in greater extent than the formers. In other words, the 1,3-bridging can be stronger in nonpolar solvents than polar ones. As a result, more rearranged product (**2a**) is formed in polar solvents; this is compatible with the fact that, in general, rearrangements during halogenations of alkenes are enhanced by utilizing polar solvents.[15] Although we do not think that the limited data available here can permit to discuss a further precise mechanism, the present results give a strong support for the intermediacy of the 1,3-bridged halonium ion such as **4** in halogenations of bicyclo[2.1.0]pentane system and reveal that halogenations of bicyclo[2.1.0]pentane system are sensitive to the solvent polarity as well as nature of the halogen used.[16]



Scheme 6.

Experimental

All the temperatures were uncorrected. The melting points were measured in sealed capillaries. The IR spectra were obtained on a Shimadzu IR-27 spectrometer. The mass spectra were taken by using a Hitachi RMS-4 mass spectrometer. The PMR and CMR spectra were obtained on Varian EM-390 and CFT-20 spectrometers, TMS being chosen as the internal standard. The microanalyses were performed by Kyoto University Elemental Analysis Center. All the reactions were carried out under nitrogen unless otherwise noted.

*Bromination of Pentacyclo[5.3.1.0^{2,6}.0^{3,5}.0^{4,9}]undecane (**1**) in CH_2Cl_2.* To a solution of **1** (292 mg; 2.0 mmol) in CH_2Cl_2 (15 ml) was added a solution of Br_2 (320 mg; 2.0 mmol) in CH_2Cl_2 (10 ml) at −78 °C in the dark. The reaction mixture was stirred for 1 h and washed with aqueous $Na_2S_2O_3$ and brine, and dried ($CaCl_2$). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane gave a mixture of *endo,exo*-4,5-dibromotetracyclo[5.3.1.0^{2,6}.0^{3,9}]undecane (**2a**), **8a** (*vide infra*), and an unidentified compound in a ratio of 91:5:4 (estimated from GLC analysis, AP 170 °C) (525 mg, 86%). Pure **2a** was obtained by preparative GLC. **2a**: mp 58—61 °C. MS *m/e* (rel intensity): 227, 225 (M^+—Br, 94, 100), 145, (63). IR (KBr): 2925, 1465, 1305, 1265, 1200, 1155, 785, 770, 725 cm^{-1}. PMR δ (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, complex m), 2.37—1.20 (8H, br. complex m). CMR δ ($CDCl_3$): 61.5 (CH), 58.0 (CH), 67.8 (CH), 47.8 (CH), 42.2 (CH_2), 41.0 (CH), 39.4 (CH), 39.4 (CH), 30.1 (CH_2). Found: C, 42.87; H, 4.88%. Calcd for $C_{11}H_{14}Br_2$: C, 43.17; H, 4.61%.

*Debromination of **2a** with $LiAlH_4$.* To a suspension of $LiAlH_4$ (54 mg; 1.42 mmol) in ether (5 ml) was added a solution of **2a** (84 mg; 0.27 mmol) in ether at room temperature. The reaction mixture was stirred for 1.5 h and quenched with sat aqueous Na_2SO_4. The organic layer was separated by decantation and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane gave tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undec-4-ene (**3**) (22 mg, 55%) which was identical with the authentic specimen.[9]

*Iodination of **1** in CH_2Cl_2.* To a solution of **1** (73 mg; 0.50 mmol) in CH_2Cl_2 (5 ml) was added a solution of iodine (127 mg; 0.50 mmol) in CH_2Cl_2 (5 ml) at room temperature in the dark. The reaction mixture was stirred for 1 h and washed with aqueous $Na_2S_2O_3$ and brine, and dried ($CaCl_2$). After filtration, the solvent was evaporated to give a mixture of *endo,exo*-4,5-diiodotetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**2b**), **3**, **7b** and **8b** (*vide infra*) in a ratio of 73:12:4:11 (PMR analysis) (187 mg). The diiodide (**2b**) has never been isolated in a pure form because of its rapid decomposition to **3** and iodine. The following data for **2b** were deduced from the measurement of the mixture. **2b**: PMR δ (CCl_4): 4.72 (1H, dd, J=6.3 and 5.4 Hz), 4.45 (1H, d, J=5.4 Hz), 3.18—1.18 (12H, br. complex m). CMR δ ($CDCl_3$): 64.2 (CH), 58.4 (CH), 47.0 (CH), 41.8 (CH_2), 41.7 (CH), 41.4 (CH_2), 41.2 (CH), 39.8 (CH), 39.5 (CH), 34.7 (CH), 29.6 (CH_2). To a suspension of $LiAlH_4$ (61 mg) in ether (5 ml) was added a solution of the above products mixture (127 mg) in ether (3 ml) at room temperature and the mixture was stirred for 1 h. Usual work-up followed by column chromatography on silica gel gave a mixture (39 mg) of **3** and **1** in a ratio of 3:1.

*Iodochlorination of **1** in CH_2Cl_2.* To a solution of **1** (219 mg; 1.50 mmol) in CH_2Cl_2 (10 ml) was added a solution of iodine chloride (244 mg; 1.50 mmol) in CH_2Cl_2 (10 ml) at room temperature in the dark. The reaction mixture was stirred for 45 min, washed with aqueous $Na_2S_2O_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue (400 mg) was distilled to give *endo*-4-chloro-*exo*-5-iodotetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**2c**) (361 mg, 78%): bp 90 °C (bath temp)/67 Pa. MS *m/e* (rel intensity): 183, 181 (M^+—I, 33, 100), 145 (30). IR (neat): 2950, 2875, 1310, 770, 750 cm^{-1}. PMR δ (CCl_4): 4.80 (1H, dd, J=6.5 and 4.5 Hz), 4.40 (1H, d, J=4.5 Hz), 3.03 (1H, q, J=6.0 Hz), 2.87—1.20 (11H, br. complex m). CMR δ ($CDCl_3$): 73.8 (CH), 63.3 (CH), 57.3 (CH), 48.1 (CH), 42.5 (CH_2), 42.3 (CH_2), 41.5 (CH), 38.9 (CH), 38.3 (CH), 32.5 (CH), 29.7 (CH). Found: C, 43.04; H, 4.78%. Calcd for $C_{11}H_{14}ClI$: C, 42.9; H, 4.57%.

endo-*4-Chlorotetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane (**2d**).* A solution of **2c** (97 mg; 0.26 mmol) and Bu_3SnH (84 mg; 0.29 mmol) in dry benzene (3 ml) was refluxed for 1 h washed with brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was sublimed (62 °C/1729 Pa) to give **2d** (29 mg, 62%): mp 79—82 °C. MS *m/e* (rel intensity): 184, 182 (M^+, 20, 61), 146 (77), 80 (88), 79 (83), 68 (100). PMR δ (CCl_4): 4.45 (1H, dt, J=10.8 and 5.7 Hz), 2.72—1.25 (14H, br. complex m). CMR δ ($CDCl_3$): 61.8 (CH), 56.6 (CH), 50.2 (CH), 49.7 (CH), 43.1 (CH_2), 43.0 (CH_2), 41.1 (CH), 39.5 (CH), 38.9 (CH), 37.8 (CH_2), 30.3 (CH_2). Found: C, 72.56; H, 8.51%. Calcd for $C_{11}H_{15}Cl$: C, 72.32; H, 8.28%.

*Iodochlorination of **3**.* To a solution of **3** (77 mg; 0.53 mmol) in CH_2Cl_2 (5 ml) was added a solution of iodine chloride (120 mg; 0.74 mmol) in CH_2Cl_2 (5 ml) at room temperature in the dark. The reaction mixture was stirred for 2 h, washed with aqueous $Na_2S_2O_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was distilled to give **2c** (53 mg, 33%) which was identical with that described above.

*Photobromination of **1**.* To a solution of **1** (59 mg; 0.47 mmol) in CCl_4 (10 ml) was added dropwise a solution of bromine (124 mg, 0.04 ml; 0.78 mmol) in CCl_4 (4 ml) at 0 °C under irradiation through soft glass filter by 300 W medium-pressure mercury arc over 2 min and the mixture was washed with aqueous $Na_2S_2O_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane gave a mixture of *endo,endo*-3,5-dibromotetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane (**7a**) and *endo,exo*-3,5-dibromotetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane (**8a**) in a ratio of 46:54 (PMR analysis) (89 mg, 72%). Each of the products was isolated by preparative GLC (AP, 180 °C). **7a**: mp 98—101 °C. MS *m/e* (rel intensity): 308, 306, 304 (M^+, 2, 5, 2), 227 (97), 225 (100), 145 (66). IR (KBr): 2925, 1480, 1295, 1210, 865, 815, 670 cm^{-1}. PMR δ (CCl_4): 4.00 (2H, s, $W_{1/2}$=8.5 Hz), 3.00 (2H, d, J=13.5 Hz), 2.85—2.30 (6H, br. complex m), 1.65 (2H, s), 1.00 (2H, d, J=13.5 Hz). CMR δ ($CDCl_3$): 48.5 (CH), 47.6 (CH), 44.3 (CH), 40.9 (CH_2), 37.9 (CH), 30.8 (CH), 30.1 (CH_2). Found: C, 43.18; H, 4.59%. Calcd for $C_{11}H_{14}Br_2$: C, 43.16; H, 4.61%. **8a**: mp 74—77 °C. MS *m/e* (rel intansity): 308, 306, 304 (M^+, 5, 10, 5), 227 (97), 225 (100), 145 (73). IR (KBr): 2930, 790, 680 cm^{-1}. PMR δ (CCl_4): 5.00 (1H, s, $W_{1/2}$=8.5 Hz), 4.63 (1H, s, $W_{1/2}$=3.0 Hz), 3.08 (1H, d, J=13.5 Hz), 2.28—1.40 (9H, br. complex m), 1.12 (1H, d, J=13.5 Hz). CMR δ ($CDCl_3$): 53.6 (CH), 53.5 (CH), 49.4 (CH), 46.6 (CH), 45.1 (CH), 41.5 (CH), 40.8 (CH_2), 36.8 (CH), 33.7 (CH), 30.6 (CH_2), 30.0 (CH_2). Found: C, 43.17; H, 4.69%. Calcd for $C_{11}H_{14}Br_2$: C, 43.16; H, 4.61%.

*Reduction of a Mixture of **7a** and **8a** with Bu_3SnH.* A mixture of **7a** and **8a** (166 mg; 0.54 mmol), Bu_3SnH (189 mg; 0.65 mmol), and $NaBH_4$ (20 mg; 0.53 mmol) in THF (10 ml) was refluxed overnight and quenched with 5% aqueous HCl. The mixture was poured onto water and extracted with hexane. The organic layer was washed with brine and dried (Na_2SO_4). After filtration, the solvent was evaporated to give **9** as a sole hydrocarbon product. The product, **9** (30 mg), was isolated by preparative GLC and shown to be identical with the authentic specimen[5] by GLC and PMR analyses.

*Photoiodination of **1**.* To a solution of **1** (73 mg; 0.50 mmol) in CH_2Cl_2 (5 ml) was added a solution of iodine (127 mg; 0.50 mmol) in CH_2Cl_2 under daylight at room temperature. The mixture was stirred for 1.5 h, washed with aqueous $Na_2S_2O_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give a mixture of *endo,endo*-3,5- and *endo,exo*-3,5-diiodotetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecanes (**7b** and **8b**) (191 mg, 96%) in a ratio of 45:56 (GLC and PMR analyses). Each of the products was isolated by preparative GLC (HVSG, 165 °C). **7b**: mp 123—125 °C. MS *m/e* (rel intensity): 400 (M^+, 4), 273 (100), 146 (88). IR (KBr): 2925, 1480, 1200, 860, 620 cm^{-1}. PMR δ (CCl_4): 3.98 (2H, s, $W_{1/2}$=8.5 Hz), 3.20 (2H, d, J=13.5 Hz), 2.90—2.25 (6H, complex m), 1.65 (2H, s), 0.95 (2H, d, J=13.5 Hz). CMR δ ($CDCl_3$): 48.3 (CH), 44.0 (CH), 40.8 (CH_2), 38.4 (CH), 30.3 (CH), 29.5 (CH_2), 18.9 (CH). Found: C, 33.01; H, 3.54%. Calcd for $C_{11}H_{14}I_2$: C, 33.02; H, 3.53%. **8b**: 115—118 °C, MS *m/e* (rel intensity): 400 (M^+, 8), 273 (100), 146 (89). IR (KBr): 2925, 1475, 1200, 765, 690, 650 cm^{-1}. PMR δ (CCl_4): 4.97 (1H, s, $W_{1/2}$=8.5 Hz), 4.63 (1H, s, $W_{1/2}$=3.0 Hz), 3.27 (1H, d, 13.5 Hz), 2.90—2.25 (6H, complex m),

2.05–1.35 (complex m), 1.08 (1H, d, J=13.5 Hz), 1.04 (1H, d, J=13.5 Hz). CMR δ ($CDCl_3$): 54.3 (CH), 47.4 (CH), 45.8 (CH), 42.6 (CH), 40.1 (CH_2), 37.5 (CH), 33.2 (CH), 32.0 (CH), 30.2 (CH_2), 29.6 (CH_2), 24.7 (CH). Found: C, 32.98; H, 3.51%. Calcd for $C_{11}H_{14}I_2$: C, 33.02; H, 3.53%.

Deiodination of a Mixture of ***7b*** *and* ***8b*** *with* $LiAlH_4$. To a suspension of $LiAlH_4$ (91 mg; 2.4 mmol) in dry ether (5 ml) was added dropwise a solution of a mixture of **7b** and **8b** (190 mg; 0.48 mmol) in dry ether (5 ml) at room temperature. The mixture was stirred overngiht and quenched with sat aqueous Na_2SO_4. Usual work-up gave **1** (60 mg, 87%).

Bromination of ***1*** *in Various Solvents in the Dark.* To a solution of **1** (10—29 mg; 0.07—0.20 mmol) in each of the solvents (2 ml) described in Table 2 was added bromine (17—50 mg; 0.11—0.31 mmol) in the solvent (1 ml) in the dark. The mixture was stirred for 1 h and analyzed by GLC (AP, 170 °C) before and/or after usual work-up. The results were summarized in Table 2.

Iodination of ***1*** *in* CCl_4 *in the Dark.* To a solution of **1** (69 mg; 0.47 mmol) in CCl_4 was added a solution of iodine (138 mg; 0.54 mmol) in CCl_4 (10 ml) in the dark at room temperature. The reaction mixture was stirred for 25 h, washed with aqueous $Na_2S_2O_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give a mixture of products (111 mg, 59%) which was shown to consist of **7b** and **8b** in a ratio of 42:58 by GLC and PMR analyses.

Iodochlorination of ***1*** *in* CCl_4 *in the Dark.* To a solution of **1** (128 mg; 0.88 mmol) in CCl_4 (5 ml) was added a solution of ICl (171 mg; 1.05 mmol) in CCl_4 (2 ml) in the dark at room temperature. The mixture was stirred for 1 h, washed with aqueous $Na_2S_2O_3$ and brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane gave **2c** (256 mg, 95%).

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References

1) In cases where there is no ambiquity, we have used trivial nomenclatures for simplicity. The IUPAC names are described in Experimental Section.

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

3) R. T. LaLonde, *J. Am. Chem. Soc.*, **87**, 4217 (1965).

4) Lambert *et al.* have reported that there is no evidence which requires a 1,3-bridged bromonium ion in bromination of bicyclo[3.1.0]hexane; J. B. Lambert, R. D. H. Black, J. H. Shun, and J. J. Papay, *J. Org. Chem.*, **35**, 3214 (1970).

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7) In the preliminary experiments, these by-products could not be detected. However, an extensive search in larger scale as well as modification of GLC analysis led to the detection of trace amount of the by-products by GLC.

8) The mass spectroscopic analysis indicated that this unidentified compound has its molecular weight more than $C_{11}H_{14}Br_2$. Because of its small quantity which was available, an extensive structural determination was not performed.

9) T. Katsushima, R. Yamaguchi, M. Kawanisi, and E. Osawa, *J. Chem. Soc., Chem. Commun.*, **1976**, 39.

10) See the first preceding paper.

11) K. J. Shea and P. S. Skell, *J. Am. Chem. Soc.*, **95**, 6728 (1973).

12) Use of UV-light resulted in a considerable decomposition of the products.

13) See the second preceding paper.

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