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Favorskii Reaction of 2-Bromobicyclo[3.3.1]nonan-3-one[1)]

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Both 2β-bromobicyclo[3.3.1]nonan-3-one (IIa) and its 2α- epimer (IIb) afforded methyl bicyclo[3.2.1]octane-6β-carboxylate (IIIa) stereoselectively in the Favorskii reaction using sodium methoxide in methanol. In the reaction using sodium methoxide in dimethoxyethane (DME) at room temperature, the stereoselectivity decreased and the product was contaminated with methyl bicyclo[3.2.1]octane-6α-carboxylate (IIIb). However, when the reaction in DME was carried out at 0 °C, IIIa was the only product.

The routes involved in these transformations were examined by using nuclear magnetic resonance spectroscopic techniques with the deuterated compounds.

Keywords——Favorskii reaction; bicyclo[3.3.1]nonane; bicyclo[3.3.1]nonan-3-one; stereoselective reaction; mechanism; bromination

The bicyclo[3.*n*.1]alkane system ($n=2, 3, 4$) is particularly interesting from the viewpoint of structure–reactivity relationships. Previously we reported practical syntheses of these systems *via* α,α′-annelation of cycloalkanones and examined the Baeyer–Villiger ring cleavage reaction of the systems. We observed remarkable inactivity of bicyclo[3.3.1]nonan-3-one (I) in the reaction, presumably because of the 7α-proton.[2)] We have therefore examined the Favorskii reaction of 2-bromobicyclo[3.3.1]nonan-3-one (II) in detail. The mechanism of the reaction is discussed.

Many studies on the Favorskii reaction of monocyclic α-haloketones have been reported, but the rearrangement of bicyclic systems has been less well studied. Some notable rearrangements have been found, however, together with other more negative results.[3)] The rearrangement in bridgehead-halogenated compounds was studied by Warnhoff *et al.*[4)] Wilt and Rasmussen,[5)] Chenier and Kao[6)] and Baretta and Waegell[7)] studied substrates having halogen at a position other than the bridgehead. The Favorskii reaction of α-halobicyclo[3.3.1]nonanes other than bridgehead-halogenated ones has not been reported.

Results and Discussion

Compound I was treated with *N*-bromosuccinimide (NBS) in carbon tetrachloride to give 2β-bromobicyclo[3.3.1]nonan-3-one (IIa), the 2α epimer (IIb), and 2β,4β-dibromobicyclo[3.3.1]nonan-3-one (IIc) in 74.5, 13.5, and 11.2% yields, respectively. The acid-catalyzed epimerization of IIa with hydrogen bromide in acetic acid gave a mixture of IIa and IIb (*ca.* 2 : 1) in high yield. The conformations of these products were assigned on the bases of their nuclear magnetic resonance (NMR) spectra.[8)] Vicinal coupling between the C_1- and C_2-protons was observed in IIb ($J=6.0$ Hz), but not in IIa. Further, the 4β-proton signal appears at δ 2.78 in IIb and at 3.16 in IIa. The downfield shift in IIa may be explained in terms of the 1,3-diaxial van der Waals deshielding effect caused by the 2β-bromine atom.[9)] The same effect

makes the signal of the C_9-axial-proton in IIa shift to δ 2.26—2.52. On the basis of these spectral data for IIa and IIb, the conformation of IIc was determined; the signal due to the C_2- and C_4-protons appeared as a singlet at δ 4.28, and the C_9-axial proton was deshielded by the two bromine atoms (δ 2.85).

The Favorskii reactions of IIa and IIb were then examined using sodium methoxide (NaOMe) in methanol (MeOH) or dimethoxyethane (DME). The results are summarized in Table I. In MeOH at room temperature (r.t.) or at 0 °C, both IIa and IIb gave methyl bicyclo[3.2.1]octane-6β-carboxylate (IIIa) stereoselectively. In DME at r.t., the major product from IIa or IIb was IIIa and the minor one was methyl bicyclo[3.2.1]octane-6α-carboxylate (IIIb). On the other hand in DME at 0°C, the only product was IIIa.

The structure of IIIa was determined by inspection of the infrared (IR), mass, and NMR spectra: in the IR spectrum an absorption due to the ester group appeared at 1734 cm^{-1}, in the mass spectrum (MS) a parent peak was found at *m/e* 168, and in the NMR spectrum all of the protons could be clearly assigned as shown in the experimental section. Furthermore, all of the carbon atoms were assigned in a ^1H–^{13}C-correlated two-dimensional NMR experiment. The structure of IIIb was determined by comparison of the ^1H-NMR spectrum of IIIa with that of IIIb. First, the 6β-proton in IIIb was more deshielded than the 6α-proton in IIIa (δ 2.98 *vs.* 2.68, respectively). Second, the *cis* coupling between the 6β-proton and the adjacent 7β-proton in IIIb was larger than the *trans* coupling between the 6α-proton and the adjacent 7β-proton in IIIa (12.0 *vs.* 5.8 Hz, respectively).[10] In addition, IIIa was treated with NaOMe in DME to give a mixture of IIIa and IIIb; this result suggests that IIIb was formed from IIIa by isomerization under the reaction conditions.

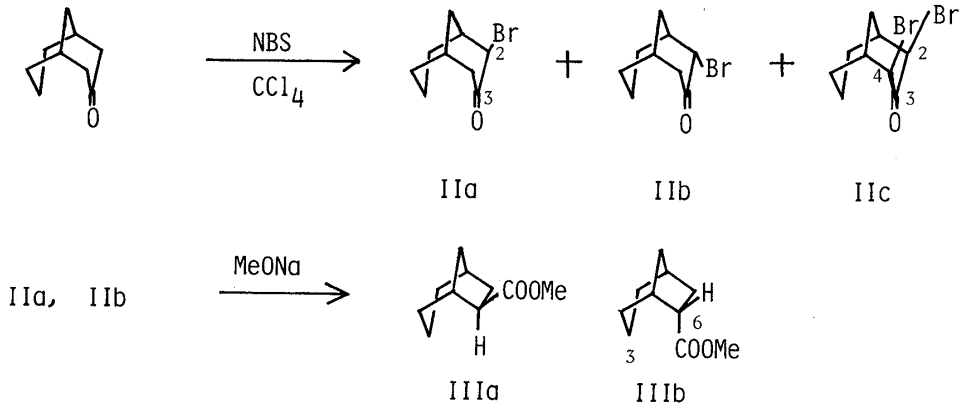

Chart 1

TABLE I. Favorskii Reaction of the Bromoketones IIa and IIb

Bromoketone	MeONa		Solvent	Temp (°C)	Ester Yield (%)	Composition (%)[a]	
	Conc. (M)	mol eq				IIIa	IIIb
IIa	0.2	2.0	MeOH	0	93.6	100	0
IIa	0.2	2.0	DME	0	79.8	100	0
IIa	0.3	5.0	MeOH	25	94.4	100	0
IIa	0.3	5.0	DME	25	79.2	87.9	12.1
IIb	0.2	2.0	MeOH	0	93.5	100	0
IIb	0.2	2.0	DME	0	69.3	100	0
IIb	0.3	5.0	MeOH	25	90.3	100	0
IIb	0.3	5.0	DME	25	78.9	86.1	13.9

a) These compositions were calculated from the ^1H-NMR spectra.

Thus, the Favorskii rearrangement of IIa and IIb was revealed to be a stereoselective reaction irrespective of solvent.[11] In order to examine the reaction path in this case, IIa was treated with d_3-NaOMe in d_4-MeOH. The product exhibited in the NMR spectrum a doublet ($J=9.0$ Hz) at δ 2.68 and a double doublet ($J=9$, 2 Hz) at δ 1.76 due to the 6α- and 7α-proton, respectively, and lacked a signal due to the 7β-proton. The MS revealed that four deuteriums were incorporated in IIIa. Furthermore, in the ^{13}C-NMR spectrum, the signal at δ 32.8 appeared as a triplet ($J_{CD}=20.1$ Hz) with decreased intensity. From these physical data, the product was suggested to be trideuteriomethyl 7β-deuteriobicyclo[3.2.1]octane-6β-carboxylate (IV).

The literature on the Favorskii reaction is voluminous. The "normal" mechanism is considered to be a cyclopropane-intermediate pathway with intervening dipolar ion species.[12] "Abnormal" Favorskii reactions have been rationalized in terms of a "semibenzylic acid rearrangement" mechanism.[13] The following products are expected from these mechanisms.

1) Ring-flip of IIa (equatorial bromine) followed by the formation of an *exo* cyclopropanone and the cleavage of the ring (retention of configuration[14]) should give IV as shown in Chart 2.

2) Formation of *endo* cyclopropanone followed by the cleavage of the ring and subsequent epimerization should give a product labeled with two deuteriums at the 6α,7α-positions.

3) Epimerization of IIa to IIb followed by semibenzylic acid rearrangement should give a product labelled with a deuterium at the C_6-position.

4) Epimerization of IIa to IIb followed by the normal mechanism should give a product labeled with two deuteriums at the $C_{6,7}$- or $C_{7,7}$-positions.

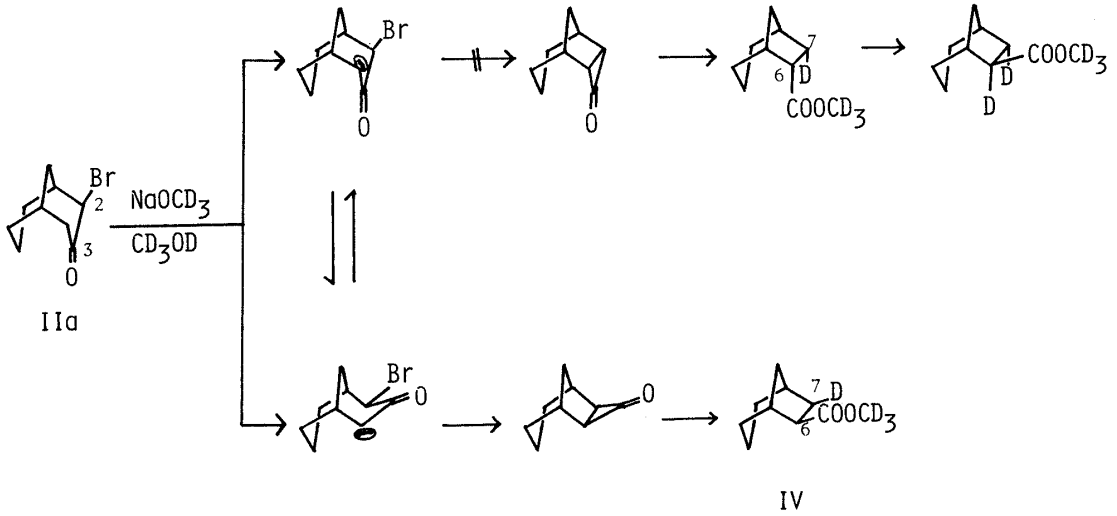

Chart 2

Meanwhile, IIb was treated with a deuterated base in the same way as described for IIa. The product was revealed, by inspection of the NMR and mass spectra, to be a mixture of trideuteriomethyl 6α,7β-dideuteriobicyclo[3.2.1]octane-6β-carboxylate (Va) and the 7,7-dideuterio analog (Vb) (1 : 1). In the NMR spectrum, Va exhibited a singlet at δ 1.76 due to the C_7-proton, and Vb showed a singlet at δ 2.68 due to the C_6-proton. In the MS, a parent peak was observed at *m/e* 173, corresponding to the compound labeled with five deuterium atoms. In the ^{13}C-NMR spectrum, the signal due to the C_7 appeared as a very weak multiplet, and the signals due to the C_1 and C_5 each as two doublets at δ 35.4 and 35.5, and 40.3 and 40.4, respectively. In this case, preferential formation[15] of an *endo* cyclopropanone ring followed by the ring cleavage (retention of configuration) and subsequent epimerization at the C_6-

position may give the 6α,7α-dideuterio ester. The epimerization of IIb to IIa followed by transformation as for IIa could give a mixture of Va and Vb as shown in Chart 3.

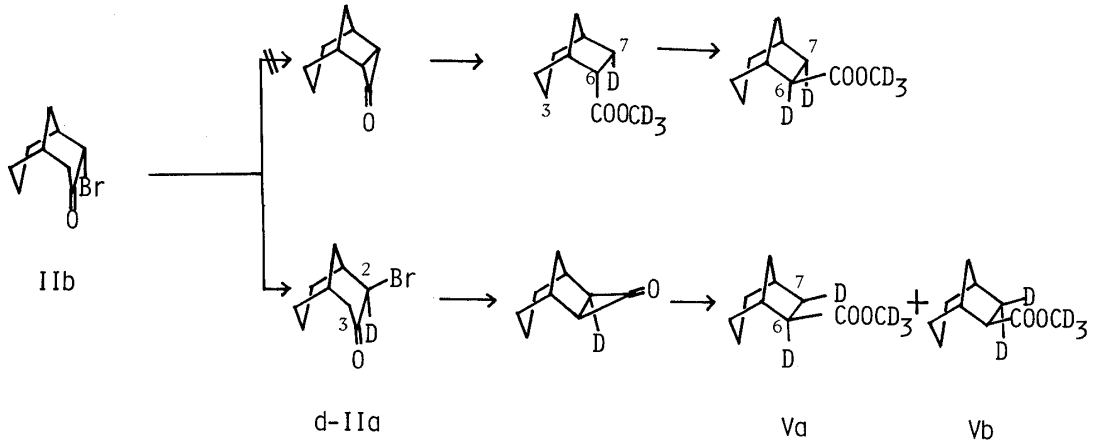

Chart 3

The results indicated that IIb does not suffer the Favorskii rearrangement by nature. Attempts to obtain IIa under various conditions *via* the epimerization of IIb failed, while an equilibrium mixture (1 : 2) of IIa and IIb could be obtained by the treatment of IIa with morpholine in DME.

It is well known[16] that the bicyclo[3.3.1]nonane system usually exists in a twin-chair conformation, which can show abnormal behavior on reduction with sodium borohydride or on Baeyer–Villiger oxidation. In the present case, the inertness of IIb to the Favorskii rearrangement and the inhibition of formation of the *endo* cyclopropanone intermediate may reflect the remarkable steric hindrance in this system.

Experimental

All melting points (taken on a Kofler block) and boiling points are uncorrected. IR spectra were taken on a JASCO A-102 grating spectrophotometer; absorption data are given in cm^{-1}. ^{1}H-NMR spectra were measured for 10% solutions on JEOL FX-200 and Varian XL-200 spectrometers with tetramethylsilane as an internal standard. The chemical shifts, coupling constants (J), and half-width ($W_{h/2}$) values are given in δ, Hz, and Hz, respectively. The 50.1 MHz ^{13}C-NMR spectra were measured on a JEOL FX-200 spectrometer. MS were measured on a JEOL D-200 (70 eV, direct inlet system). Gas-liquid partition chromatography (GLC) was carried out on a Shimadzu GC-6AM instrument with a stainless steel column (3 mm × 3 m) packed with 5% SE-30. The N_2 gas flow was 40 ml/min. Column chromatography was performed on Fuji Devison silica gel (SiO_2) BW-200. All the organic extracts were dried over anhyd. $MgSO_4$ prior to evaporation under reduced pressure.

Bromination of Bicyclo[3.3.1]nonan-3-one (I)——A mixture of I[2] (1.00 g, 7.25 mmol), NBS (freshly recrystallized from water, 1.94 g, 10.9 mmol), benzoyl peroxide (0.1 g), and CCl_4 was refluxed for 4.5 h. White succinimide began to precipitate after 10 min, and a pale yellow mixture was obtained after the full heating period. The mixture was cooled in an ice-bath and then filtered. The precipitate was washed with chilled CCl_4 (3 × 15 ml). The combined filtrate was washed with 10% $NaHCO_3$(2 × 10 ml) and once with H_2O. A yellow oil (1.88 g) obtained after evaporation of the solvent was purified through an SiO_2 column. 2β,4β-Dibromobicyclo[3.3.1]nonan-3-one (IIc, 0.24 g, 11.2%), 2β-bromobicyclo[3.3.1]nonan-3-one (IIa, 1.17 g, 74.5%), and 2α-bromobicyclo[3.3.1]nonan-3-one (IIb, 0.21 g, 13.5%) were eluted successively with benzene.

IIa: Oil, bp 94—97 °C (4 mmHg). IR (neat): $\nu_{C=O}$ 1708. ^{1}H-NMR ($CDCl_3$): 1.16—1.58 (2H, m), 1.60—1.76 (3H, m), 1.78—1.92 (2H, m), 2.16—2.52 (3H, m, 1α-,5α-, and 4α-H), 2.26 (1H, ddd, J = 16.5, 4, 2, C_9-*syn*-H), 3.16 (1H, dd, J = 16.5, 6, 4β-H), 4.32 (1H, s, 2α-H). ^{13}C-NMR ($CDCl_3$): 18.9 (t, C_7), 28.6 (t, C_9), 32.0 (t, C_6 or C_8), 32.2 (d, C_5), 32.8 (t, C_8 or C_6), 40.2 (d, C_1), 42.7 (t, C_4), 56.1 (d, C_2), 207.8 (s, C_3). *Anal.* Calcd for $C_9H_{13}BrO$: C, 49.79; H, 6.04. Found: C, 49.71; H, 5.82.

IIb: bp < 130 °C (4 mmHg), mp 41—43 °C. IR (KBr): $\nu_{C=O}$ 1715. ^{1}H-NMR ($CDCl_3$): 1.02—1.32 (1H, m), 1.34—1.76 (4H, m), 2.02 (1H, ddd, J = 14, 6, 3), 2.10—2.26 (2H, m), 2.38 (1H, br s, C_5-H), 2.52 (1H, ddd, J = 16.5, 2.5, 2, 4α-H), 2.58 (1H, br s, C_1-H), 2.78 (1H, dd, J = 16.5, 6, 4β-H), 5.15 (1H, d, J = 6, 2β-H). ^{13}C-NMR ($CDCl_3$): 18.7 (t, C_7), 28.3 (t, C_9), 32.8 (d, C_5), 32.9 and 35.4 (each t, C_6 and C_8), 41.7 (d, C_1), 47.8 (t, C_4), 63.1 (d, C_2), 205.9 (s, C_3). *Anal.*

Calcd for $C_9H_{13}BrO$: C, 49.79; H, 6.04. Found: C, 49.68; H, 5.95.

IIc: mp 123—124 °C (from hexane). IR (KBr): $\nu_{C=O}$ 1710. ^{1}H-NMR ($CDCl_3$): 0.92—1.28 (2H, m, 7α-, C_9-*anti*-H), 1.38—1.99 (5H, m), 2.54 (2H, br s, $W_{h/2}=9$, C_1-, C_5-H), 2.85 (1H, d, $J=12$, C_9-*syn*-H), 4.28 (2H, s, >CH-Br). ^{13}C-NMR ($CDCl_3$): 17.3 (d, C_7), 22.6 (t, C_9), 31.5 (t, C_6, C_8), 38.7 (d, C_1, C_5), 48.6 (d, C_2, C_4), 200.8 (s, C_3). *Anal.* Calcd for $C_9H_{12}Br_2O$: C, 36.52; H, 4.09. Found: C, 36.40; H, 3.91.

Isomerization of IIa——HBr gas (2.82 g, 34.9 mmol) was gently bubbled into a solution of IIa (3.70 g, 17.1 mmol) in glacial AcOH (20 ml) and CCl_4 (60 ml) at 0 °C. The solution was allowed to stand at r.t. for 3 d, then poured into ice-water (300 ml) and extracted with Et_2O (80 ml × 4). A crude mixture of IIa and IIb was obtained after removal of the solvent as a brown oil. The mixture was fractionated through an SiO_2 column. IIa (2.43 g, 65.5%) and IIb (1.06 g, 28.5%) were eluted with hexane and benzene, respectively. Their spectral data were identical with those of authentic samples.

Favorskii Reaction of IIa (Table I)——i) In MeOH: A methanolic solution of IIa (504 mg, 2.32 mmol) was added at 0 °C to a methanolic solution (30 ml) of NaOMe (0.2 M) and the mixture was stirred for 2 h at 0 °C. The resulting solution was neutralized with glacial AcOH and then dry Et_2O (40 ml) was added to give a precipitate of sodium acetate. The filtrate was evaporated to give a colorless oil (371 mg), which was fractionated through an SiO_2 column. IIIa (365 mg, 93.6%) was obtained from the benzene fraction. Methyl bicyclo[3.2.1]octane-6β-carboxylate (IIIa): bp < 125 °C (9 mmHg). IR (film): $\nu_{C=O}$ 1734, δ_{c-o} 1195, 1173, 1145. MS *m/e* (%): 168 (M^+, 3), 137 ($M^+ - OMe$, 5), 87 ($CH_3-\overset{+}{C}H-COOMe$, 100). ^{1}H-NMR ($CD_3OD$): 1.34 (1H, d, $J=11.5$, C_8-*syn*-H), 1.36—1.60 (6H, m, C_2-, C_3-, and C_4-H), 1.68 (1H, ddd, $J=11.5$, 5, 5, C_8-*anti*-H), 1.76 (1H, ddd, $J=13$, 9, 2, 7α-H), 2.00 (1H, ddd, $J=13$, 7, 5.8, 7β-H), 2.23 (1H, br s, C_1-H), 2.33 (1H, br s, C_5-H), 2.68 (1H, dd, $J=9$, 5.8, 6α-H). ^{13}C-NMR (CD_3OD): 20.0 (t, C_3), 32.8 and 33.2 (each t, C_2 and C_4), 33.9 (t, C_7), 36.8 (d, C_1), 38.8 (t, C_8), 41.5 (d, C_5), 47.4 (d, C_6), 52.0 (q, OMe), 178.8 (s, C=O). High-resolution MS, Calcd for $C_{10}H_{16}O_2$: 168.1150. Found: 168.1152.

ii) In DME: a) A DME solution of IIa (513 mg, 2.37 mmol) was added at 0 °C to a well-stirred suspension of NaOMe (255 mg, 4.73 mmol) in DME (25 ml), and the mixture was stirred for a further 5 h at 0 °C. The reaction mixture was worked up as described above to give IIIa in 79.8% yield. b) A solution of IIa (715 mg, 3.29 mmol) in DME (10 ml) was added at 0 °C to a well-stirred suspension of NaOMe (890 mg, 16.5 mmol) in DME (60 ml), and the mixture was stirred for 2 h at r.t. The reaction mixture was worked up as usual to give a mixture of IIIa and IIIb (87.9 : 12.1, 79.2%). MS *m/e* (%): 168 (M^+, 2), 137 ($M^+ - OMe$, 4), 136 ($M^+ - MeOH$, 6), 87 ($CH_3-\overset{+}{C}H-COOMe$, 100). ^{1}H-NMR of the mixture (CD_3OD): Signals due to IIIb were selected. 2.98 (1H, ddd, $J=12$, 9, 9, 6β-H), 3.68 (3H, s, OMe). ^{13}C-NMR (CD_3OD): the signals were selected from the spectrum of the mixture. 19.6, 30.0, 30.9, 33.8, 36.0, 40.1, 41.5, and 51.9.

Other results for IIa and IIb are given in Table I.

Attempts to Isomerize IIa to IIb——Morpholine (freshly distilled, 1.85 ml, 21.4 mmol) was added to a solution of IIa (930 mg, 4.29 mmol) in dry DME (10 ml) at 0°C. The mixture was stirred for 66 h at r.t. The resulting suspension was carefully acidified with 10% sulfuric acid, and extracted with Et_2O (20 ml × 4). The organic layer was washed with brine and then dried. Removal of the solvent gave a pale yellow oil (873 mg), which was fractionated through an SiO_2 column. IIa and IIb were eluted successively with benzene. IIa: 61 mg, 8.7%. IIb: 200 mg, 26%, mp 41—43 °C.

Attempts to Isomerize IIIa to IIIb——Powdered NaOMe (9 mg, 0.16 mmol) was added to a solution of IIIa (80 mg, 0.48 mmol). The suspension was stirred for 4 h at r.t. and chilled to 0 °C followed by neutralization with glacial AcOH. The precipitate was filtered off and washed with Et_2O (5 ml × 4). Concentration of the combined solution gave a colorless oil (84 mg), which was fractionated through an SiO_2 column. A mixture of IIIa and IIIb (77 mg, 83 : 17) was obtained as a colorless oil.

Favorskii Reaction of IIa and IIb with d_3-MeONa in CD_3OD——i) On IIa: A 0.3 M solution of d_3-MeONa in CD_3OD (2.3 ml, 0.69 mmol) was added to a solution of IIa (50 mg, 0.23 mmol) under ice-cooling, and the mixture was stirred for 1 h at r.t. The pale yellow mixture was cooled on an ice bath and neutralized with glacial AcOH. Then dry Et_2O (10 ml) was added to precipitate NaOAc, which was removed by filtration and washed with dry Et_2O (10 ml). Concentration of the combined solution gave a pale yellow oil, which was purified through an SiO_2 column with benzene as an eluent, then microdistilled to give trideuteriomethyl 7β-deuteriobicyclo[3.2.1]octane-6β-carboxylate (IV). 33 mg (82.5%) bp < 130 °C (9 mmHg). IR (film): ν_{C-D} 2250, 2180, 2120, 2075, $\nu_{C=O}$ 1730. MS *m/e*(%): 172 (M^+, 2), 138 ($M^+ - OCD_3$, 3), 137 (2), 129 (2), 110 (5), 91 ($CDH_2-\overset{+}{C}H-COOCD_3$, 100). ^{1}H-NMR ($CD_3OD$): 1.76 (1H, dd, $J=9$, 2, 7α-H), 2.68 (1H, d, $J=9$, 6α-H). ^{13}C-NMR ($CDCl_3$): 19.2 (t, C_3), 31.8 and 32.3 (each t, C_2 or C_4), 32.8 (t, $J_{CD}=20.1$, C_7), 35.4 (d, C_1), 38.0 (t, C_8), 40.4 (d, C_5), 46.2 (d, C_6).

ii) On IIb: When treated as described in i), IIb (50 mg, 0.23 mmol) afforded a mixture (37 mg, 92.5%) of trideuteriomethyl 6α,7β-dideuteriobicyclo[3.2.1]octane-6β-carboxylate (Va) and trideuteriomethyl 7,7-dideuteriobicyclo[3.2.1]octane-6β-carboxylate (Vb) (Va : Vb = 1 : 1) as a colorless oil. IR (film): ν_{C-D} 2230, 2175, 2100, 2060, $\nu_{C=O}$ 1725. ^{1}H-NMR (CD_3OD): 1.76 (0.5H, br s, 7β-H of Va), 2.68 (0.5H, s, 6α-H of Vb). MS *m/e*(%): 173 (M^+, 2), 139 ($M^+ - OCD_3$, 3), 138 (2), 111 (5), 92 ($CDH_2-\overset{+}{C}D-COOCD_3$ or $CD_2H-\overset{+}{C}H-COOCD_3$, 100), 91 (33). ^{13}C-NMR ($CDCl_3$): 19.2 (t, C_3), 31.8 and 32.3 (each t, C_2 or C_4), 32.7 (m, C_7), 35.4 and 35.5 (each d, C_1), 38.0 (t, C_8), 40.3 and 40.4 (each d, C_5), 46.2 (d, C_6), 177.6 (s).

References and Notes

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