Synthesis and Properties of Bridgehead-substituted Bicyclo[*n*.2.2] Bridgehead Alkenes

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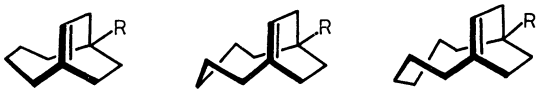
The bridgehead-substituted bicyclo[*n*.2.2] bridgehead alkenes (**1b—3b**) (**1**, $n=4$; **2**, $n=5$; **3**, $n=6$; **b**, R=OAc) were synthesized based on the oxidative decarboxylation of [*n*.2.2]propellanecarboxylic acids with lead tetraacetate. The parent alkene (**1a—3a**) (**a**, R=H) and other bridgehead-substituted derivatives (**1c—3c** and **1d—3d**) (**c**, R=OH; **d**, R=Cl) were prepared from **1b—3b**. The examination of the ^{13}C NMR chemical shifts of **1a—c**, **2a—c**, and **3a—c** indicates the presence of electronic interaction between the bridgehead double bond (C_γ) and the opposite bridgehead carbon (C_α), being the homoallylic position of the double bond. From the product study and the kinetic results of the solvolysis of the bridgehead chlorides **1d—3d**, it is indicated that the homoallylic participation of the strained bridgehead double bond to the carbonium ion center located at the opposite bridgehead position operates in the solvolysis of **1d** and **2d**. It may be, therefore, concluded that highly strained bridgehead alkenes, especially, bicyclo[4.2.2]decene system, show remarkable homoallylic type α,γ-interaction both in the ground state and in the transition state (carbonium ion).

There has been considerable interest in the chemistry of strained bridgehead olefins, especially with regard to the development of new efficient methods providing an entry to the highly strained molecules and the examination of specific physical properties and chemical reactivities associated with the distortion imposed on the double bond.[1] In a continuation of the study on the transformation of readily available [*n*.3.2]propellanones into other important carbocyclic ring systems,[2] we have recently developed a synthetic entry to the bicyclo[*n*.2.2]bridgehead alkenes (**1b—3b**) having an acetoxyl group at the opposite bridgehead position based on the oxidative decarboxylation of [*n*.2.2]propellanecarboxylic acids (**4a—6a**) with lead tetraacetate.[3a] In this connection, we wish to report here on the synthesis of bicyclo[*n*.2.2] bridgehead alkenes (**1a—3a**) and the bridgehead-substituted derivatives (**1c—3c**) and (**1d—3d**) from **1b—3b**, on the physical properties, that is, ^{13}C NMR spectra of **1a—3a**, **1b—3b**, and **1c—3c**, and on the chemical reactivities in the solvolysis of the bridgehead chlorides **1d—3d**.[3]

Although the ^{13}C NMR spectra of conformationally rigid polycarbocyclic compounds possessing bridgehead substituents have been extensively studied,[4] little is known concerning those of highly strained bridgehead olefins.[5] It is, therefore, of particular interest to examine the ^{13}C NMR chemical shifts of a series of the bridgehead-substituted bridgehead alkenes **1a—c**, **2a—c**, **3a—c** in connection with the effect of both oxygen substituents at the bridgehead position and the ring size (*n*) on the chemical shifts. The examination of the chemical shifts of **1a—c**, **2a—c**, and **3a—c** obviously indicated the presence of electronic interaction between the bridgehead double bond and the opposite bridgehead carbon, being the homoallylic position of the double bond. These results prompted us to investigate the homoallylic interaction between the bridgehead double bond and the carbonium ion center located at the opposite bridgehead position in the solvolysis of the bridgehead chlorides **1d—3d**.[6] As a result, the product study and the kinetic results of the solvolysis demonstrated the presence of the



1a—d **2a—d** **3a—d**

a, R=H; **b**, R=OAc; **c**, R=OH; **d**, R=Cl

homoallylic participation of the strained double bond to the carbonium ion center, especially in the case of the most strained bicyclo[4.2.2]decene system (**1**).

Results and Discussion

Synthesis. The entry into the bridgehead-substituted bicyclo[*n*.2.2] bridgehead alkene systems was based on the oxidative decarboxylation of [*n*.2.2]-propellanecarboxylic acids **4a—6a** with lead tetraacetate, which were prepared from [*n*.3.2]propellanones[7] by the ring contraction involving the photochemical Wolff rearrangement. The reaction of **4a—6a** with lead tetraacetate was carried out in the presence of pyridine in benzene solution at 80 °C for 1 h. The [6.2.2]propellane **6a** gave the intended allylcarbinyl type bicyclic acetate **3b**, having a bridgehead double bond, in 81% yield. In the case of the [5.2.2]propellane **5a**, the cyclopropylcarbinyl type tricyclic acetate (**8b**), however, was obtained as the major product in 60% yield along with 13% of the desired bridgehead olefin **2b** and small amounts (3%) of [5.2.2]propellene (**10**). Moreover, the [4.2.2]propellane **4a** afforded the tricyclic acetate (**7b**) exclusively in 68% yield together with 5% of [4.2.2]propellene (**9**), but the intended olefin **1b** was not produced at all. These products may be derived from the rearrangement of the initially formed cyclobutyl cation to allylcarbinyl and/or cyclopropylcarbinyl ones. In order to transform the tricyclic acetates **7b** and **8b** into the corresponding bridgehead alkenes **1b** and **2b**, we first examined the

9 **10**

vapor phase thermolysis of **7b** and **8b** at 350 °C under nitrogen stream. Although the thermolysis proceeded in high efficiency to give **1b** and **2b**, this process seems to be not suited for large-scale preparation of **1b** and **2b**. We next tried, therefore, the acid catalyzed rearrangement of **7b** and **8b**. After many trials, it appeared that simple treatment of **7b** and **8b** with acetic acid was the best way for this purpose. The bridgehead alcohols **1c**—**3c** were prepared by the lithium aluminum hydride reduction of **1b**—**3b**, and the bridgehead chlorides **1d**—**3d**, being the substrates required for solvolysis experiments, were derived from the reaction of **1c**—**3c** with thionyl chloride or phosphoryl chloride. The preparation of the unsubstituted hydrocarbons **1a**—**3a** was not straightforward. Thus **1a** was prepared by the elimination of acetic acid by means of the vapor phase thermolysis of the saturated acetate (**11b**) (76%) or by the dehydration through treating the saturated alcohol (**11c**) with thionyl chloride/pyridine (74%), which were derived by the diimide reduction of **1b** and **1c**, respectively.[8] Although the similar reduction of **2c** afforded **12c**, those of **2b**, **3b**, and **3c**, however, were unsuccessful.[9,10] The bridgehead alkene **2a** was prepared, therefore, by the dehydration of **12c** (80%) or by the thermolysis of **12b** (82%) which was obtained by the acetylation of **12c** using 4-dimethylaminopyridine/acetic anhydride.[11] On the other hand, **3a** was prepared by the reduction of the chloride **3d** with lithium/*t*-butyl alcohol in 67% yield. All the synthetic scheme is summarized in Scheme 1.

^{13}C NMR Spectra. The ^{13}C NMR chemical shifts for the bridgehead-substituted bridgehead alkenes **1a**—**c**, **2a**—**c**, and **3a**—**c** are listed in Table 1. Though it was impossible to assign all the carbons, α carbon, olefinic γ carbon, and olefinic δ carbon (Fig. 1) were unequivocally assigned on the basis of

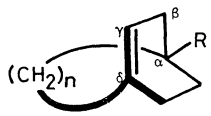
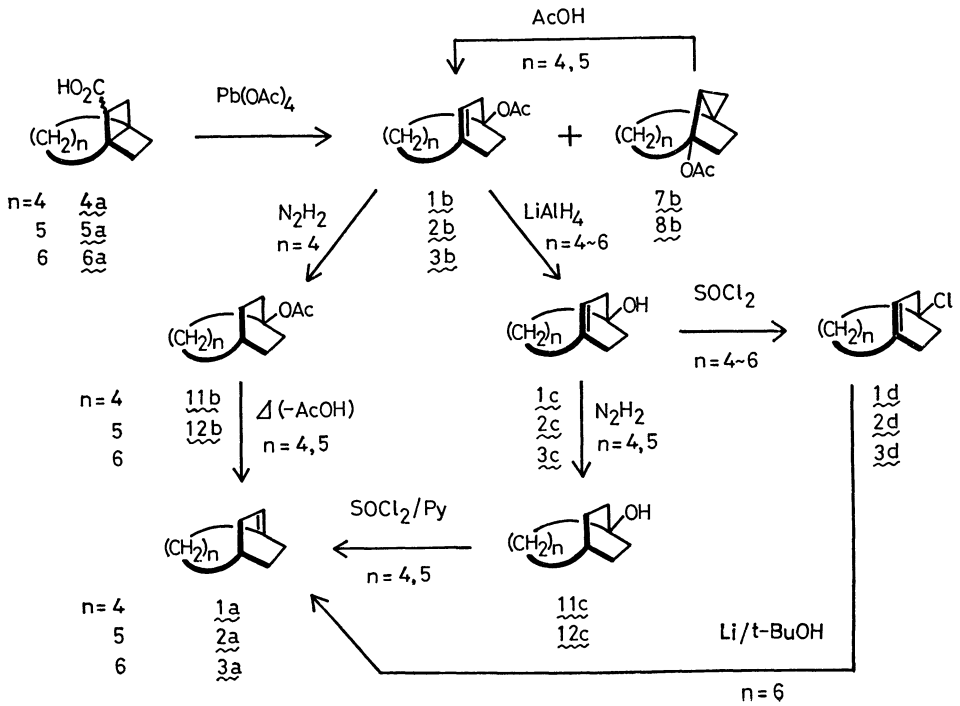


Fig. 1.

the multiplicities of the off-resonance decoupled spectra. Therefore, the discussion should be focused on the chemical shifts of the above three carbons. The substituent effects in each ring system, *i.e.*, the chemical shift differences between the alkenes having same ring system and different bridgehead substituents taking the hydrocarbons **1a**—**3a** as standard, are listed in Table 2, and the ring size effects, *i.e.*, the chemical shift differences between the alkenes having same substituent and different ring systems taking bicyclo[6.2.2]-dodecene systems **3a**—**3c** as standard, are in Table 3. As shown in Table 2, the magnitude of the substituent effects on each carbon is in the order α effects> γ effects>δ effects, as might be expected from the distance from the substituents to each carbon. The magnitude of α substituent effects, which are directly related to the electronegativity of oxygen, as well as the small degree of δ effects observed for **1b**—**c**, **2b**—**c**, and **3b**—**c** are in accord with the cases of other bridgehead substituted alkanes.[4] However, by contrast to the small downfield shifts for γ carbons in the bridgehead substituted alkanes,[4] the remarkable upfield shift was observed for the γ carbons in the present bridgehead alkenes. Thus, for example, the γ carbon resonances of **1b** and **1c** appeared 4.99 and 3.98 ppm higher field than that of **1a**. As can be seen in Table 3, most of α, γ, and δ carbons of **1a**—**c** and **2a**—**c**, except for γ carbons of **2a**—**c**, were deshielded compared with those of **3a**—**c**, which indicated the increase of steric strain with decrease in the ring size (n).



Scheme 1.

Table 1. ^{13}C NMR Chemical shifts of bicyclo[n.2.2] bridgehead alkenes **1a—c**, **2a—c**, and **3a—c**[a)]

Compd	R	C_α	C_γ	C_δ	Other carbons
1a	H	36.51	126.86	141.97	38.70, 35.37, 32.89, 29.48, 28.87, 27.74, 26.84
1b	OAc	88.70	121.87	143.00	170.70, 40.02, 37.09 (2C), 32.24, 30.14, 27.50, 25.49, 22.65
1c	OH	79.02	122.88	141.76	44.83, 40.77, 38.05, 35.94, 27.74, 26.92, 26.19
2a	H	30.82	122.80	138.92	37.20, 36.02, 33.58, 28.63, 28.43, 27.09, 24.69, 24.16
2b	OAc	86.60	119.72	140.71	170.60, 42.47, 37.33, 36.55, 30.24, 29.40, 27.99, 27.64, 24.85, 22.70
2c	OH	75.13	120.77	139.81	46.29, 41.34, 36.47, 33.14, 29.28, 28.26, 27.13, 25.75
3a	H	30.33	124.06	138.23	38.38, 35.90, 29.89, 29.16, 27.61 (2C), 27.49, 24.89 (2C)
3b	OAc	86.06	120.55	138.60	170.60, 39.34, 37.33 (2C), 35.76, 32.39, 28.03 (2C), 25.73 (2C), 22.80
3c	OH	73.78	121.46	138.27	44.55, 38.74, 37.40 (2C), 35.57, 28.87, 27.41 (2C), 26.35

a) Measured at −11——14 °C in $CDCl_3$ solution and the shifts are in ppm with respect to internal Me_4Si.

Table 2. Substituent effects on the ^{13}C NMR chemical shifts for bicyclo[n.2.2] bridgehead alkenes[a)]

Compd	Substituent	C_α	C_γ	C_δ
1b[b)]	OAc	52.19	−4.99	1.03
1c[b)]	OH	42.51	−3.98	−0.21
2b[c)]	OAc	55.78	−3.08	1.79
2c[c)]	OH	44.31	−2.03	0.89
3b[d)]	OAc	55.77	−3.51	0.37
3c[d)]	OH	43.45	−2.60	0.04

a) Positive shifts are to lower field and negative shifts are to higher field. b) Relative to **1a**. c) Relative to **2a**. d) Relative to **3a**.

Table 3. Ring size effects on the ^{13}C NMR chemical shifts for bicyclo[n.2.2] bridgehead alkenes[a)]

Compd	Substituent	C_α	C_γ	C_δ
1a	H	6.18	2.80	3.64
1b	OAc	2.64	1.32	4.40
1c	OH	5.24	1·42	3.49
2a	H	0.49	−1.26	0.69
2b	OAc	0.54	−0.83	2.11
2c	OH	1.35	−0.69	1.54

a) Values refer to the differences between the chemical shifts of a given compound and those of **3a—3c** having the same bridgehead substituent. Positive shifts are to lower field and negative shifts are to higher field.

The most significant feature in the ^{13}C NMR spectra of the bicyclo[n.2.2] bridgehead alkenes is the remarkable shielding γ effects observed in **1b—c**, **2b—c**, and **3b—c**. The γ anti shielding effects is well known for some alicyclic systems and several possible mechanisms have been posturated for interpretation of the effect such as electrostatic field effect,[12)] back-lobe interaction of sp^3 orbitals on C_γ with that of C_α-hetero atom bond,[13)] and α,γ-hyperconjugative type interaction of free-electron pairs on hetero atom.[14)] The present γ effect may also be accounted by one or more

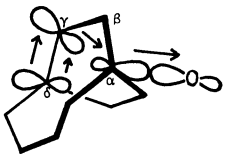
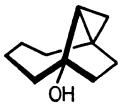


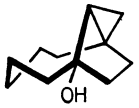
Fig. 2.

of the above explanations, because the molecular framework of the bridgehead alkenes are considerably deformed so that C_α and C_γ are in close proximity compared with unstrained saturated bicyclic systems. However, in view of the solvolysis behavior of the bridgehead chlorides **1d** and **2d** described later, we think it more attractive to ascribe the present γ effect to the interaction of the back-lobe of sp^3 orbital of C_α-oxygen bond with C_γ p orbital of the distorted bridgehead double bond, as shown in Fig. 2. Moreover, inspection of molecular models suggests that, in agreement with the observed effects, such interaction may be most pronounced in bicyclo[4.2.2]decene system (**1**) because of favorable geometry of the two orbitals for the interaction.

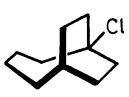
Solvolysis of the Bridgehead Chlorides ***1d—3d.*** From the standpoint of facility in the identification of the solvolysis products, the hydrolysis of the bridgehead chlorides **1d—3d** was attempted, because the expected hydrolysis products, that is, the bridgehead alcohols **1c—3c** and **7c—8c** should be readily available. The product study of the solvolysis of **1d—3d** was, therefore, carried out in 80% (v/v) acetone–water containing 2,6-lutidine buffer. Whereas the solvolysis of **3d** gave only the unrearranged alcohol **3c**, **1d** afforded the rearranged cyclopropylcarbinyl type alcohol **7c** as a sole product, and, in addition, **2d** gave 87% of the rearranged alcohol **8c** and 13% of the unrearranged one **2c**. The solvolysis rates of **1d—3d** were determined in ethanol solvent, because, unfortunately,



7c



8c



11d

Table 4. Kinetic data for the ethanolysis of the bridgehead chlorides **1d—3d** and **11d**

Chloride	Temp[a] °C	k[b] s^{-1}	k_{rel}	ΔH^* kcal mol^{-1}	ΔS^* eu
1d	25.0	1.52×10^{-4}	214	23.9	−1.8
	20.0	7.50×10^{-5}			
2d	33.0	1.96×10^{-4}			
	25.0	7.44×10^{-5}	105	21.4	−5.9
3d	33.0	3.00×10^{-5}			
	25.0	1.07×10^{-5}	15.1	22.8	−5.0
11d	55.0	4.27×10^{-5}			
	40.0	6.07×10^{-6}		25.9	+4.5
	25.0[c]	7.10×10^{-7}	1.0		

a) ±0.1 °C. b) The deviations are within 6%. c) Extrapolated value.

Table 5. Spectral and analytical data for the bridgehead alkenes **1a—3a**, **1b—3b**, **1c—3c**, and **1d—3d** and the cyclopropylcarbinyl type tricyclic compounds **7b**, **8b**, **7c**, and **8c**

Compd	IR $\tilde{\nu}$/cm^{-1}	MS (m/e)	^{1}H NMR[a] δ/ppm	Found (Calcd) C (%)	H (%)
1a[b,c]	3030, 1640	136 (M^+)	1.00—2.60 (m, 15H), 5.68 (t, J=7 Hz, 1H)		
2a[d]	3030, 1640	150 (M^+)	1.00—2.80 (m, 17H), 5.46—5.65 (m, 1H)	87.71 (87.92)	12.00 (12.08)
3a[e]	3030, 1640	164 (M^+)	0.90—2.60 (m, 19H), 5.66 (broad d, J=7 Hz, 1H)	87.73 (87.40)	12.27 (12.15)
1b[f]	3040, 1710, 1220	194 (M^+, trace), 134 (M^+−AcOH)	1.35—2.80 (m, 17H, s at 1.88), 5.32—5.56 (m, 1H)	74.55 (74.19)	9.54 (9.34)
2b[g]	3040, 1710, 1225	208 (M^+, trace), 148 (M^+−AcOH)	1.05—2.60 (m, 19H, s at 1.75), 5.36 (broad d, J=8 Hz, 1H)	75.08 (74.96)	9.68 (9.74)
3b[h]	3040, 1710, 1230	222 (M^+, trace), 162 (M^+−AcOH)	1.15—2.80 (m, 21H, s at 1.71), 5.32 (broad d, J=8 Hz, 1H)	75.20 (75.63)	9.93 (9.97)
1c[i]	3350, 3030, 1065, 1030	152 (M^+)	1.00—2.65 (m, 15H), 5.32—5.56 (m, 1H)	78.82 (78.89)	10.76 (10.59)
2c[i]	3350, 3030, 1060, 1020	166 (M^+)	1.05—2.70 (m, 17H), 5.48 (broad d, J=7 Hz, 1H)	79.21 (79.46)	10.78 (10.92)
3c[j]	3350, 3030, 1010	180 (M^+, trace), 162 (M^+-H_2O)	0.90—2.70 (m, 19H), 5.48 (broad d, J=6 Hz, 1H)	79.63 (79.94)	11.10 (11.18)
1d[k]	3030, 870, 730	170 (M^+)	0.95—2.80 (m, 14H), 5.25—5.40 (m, 1H)	70.53 (70.37)	8.89 (8.86)
2d[l]	3030, 870, 730	184 (M^+)	0.80—2.90 (m, 16H), 5.25 (broad d, J=8 Hz, 1H)	71.64 (71.52)	9.26 (9.28)
3d[m]	3030, 880, 730	198 (M^+)	0.90—2.80 (m, 18H), 5.26 (broad d, J=8 Hz, 1H)	72.94 (72.52)	9.64 (9.64)
7b	3050, 1720, 1230	194 (M^+, trace), 134 (M^+−AcOH)	0.92 (d, J=6 Hz, 2H), 1.13—2.60 (m, 16H, s at 1.74)	74.01 (74.19)	9.42 (9.34)
8b	3050, 1720, 1235	208 (M^+, trace), 148 (M^+−AcOH)	0.36—0.72 (m, 2H), 1.05—2.60 (m, 18H, s at 1.76)	74.77 (74.96)	9.86 (9.68)
7c[n]	3350, 3050, 1100, 1030	152 (M^+)	0.62 (t, J=7 Hz, 1H), 0.95 (d, J=7 Hz, 1H), 1.05—2.60 (m, 14H)	78.53 (78.89)	10.60 (10.59)
8c[o]	3350, 3050, 1070, 1020	166 (M^+)	0.41 (2d, J=8 Hz, 4 Hz, 1H), 0.60 (t, J=4 Hz, 1H), 1.05—2.40 (m, 16H)	79.13 (79.46)	11.13 (10.92)

a) ^{1}H NMR spectra of **1a—3a** were measured in $CDCl_3$ solutions and those of the other compounds were in C_6D_6 solutions. b) Since **1a** was highly sensitive to oxygen, correct analytical data could not be obtained. c) Mp 33—35 °C. d) Mp 30—32 °C. e) Bp 50—60 °C (bath temp)/20 mmHg. f) Bp 75—78 °C/0.5 mmHg. g) Bp 80—83 °C/0.2 mmHg. h) Bp 85—87 °C/0.3 mmHg. i) Semisolid. j) Mp 84—85 °C. k) Bp 55—65 °C (bath temp)/1 mmHg; ^{13}C NMR ($CDCl_3$) δ 141.46 (s), 123.31 (d), 76.73 (s), 46.55 (t), 41.64 (t), 38.23 (t), 36.40 (t), 28.97 (t), 27.24 (t), 26.79 (t). l) Bp 75—85 °C (bath temp)/2 mmHg; ^{13}C NMR ($CDCl_3$) δ 139.53 (s), 121.25 (d), 75.37 (s), 47.67 (t), 43.82 (t), 36.34 (t), 35.21 (t), 29.44 (t), 28.79 (t), 26.80 (t), 26.44 (t). m) Bp 102—105 °C/4 mmHg; ^{13}C NMR ($CDCl_3$) δ 138.07 (s), 122.27 (d), 75.49 (s), 46.50 (t, 2C), 37.36 (t, 3C), 28.55 (t), 27.13 (t), 26.92 (t, 2C). n) Mp 87—89 °C. o) Mp 90—92 °C.

the hydrolysis rates of **1d**—**3d** were too rapid to measure.[15] The rates of ethanolysis of **1d**—**3d** buffered with 10% (v/v) of 2,6-lutidine were listed in Table 4.[16] For comparison, the ethanolysis rates of the saturated chloride (**11d**) were also determined. As shown in Table 4, **1d** was most reactive and was solvolyzed at a rate 214 times faster than the corresponding saturated chloride **11d**. The solvolysis rate of **2d** was about a half of that of **1d** but was still considerably greater than those of **3d** and **11d**. The product study and the kinetic results indicate clearly the presence of the homoallylic participation of the strained bridgehead double bond to the carbonium ion center located at the opposite bridgehead position in bicyclo[4.2.2]decene and bicyclo[5.2.2]undecene systems, although it may be conceivable that relief of large strain in the ground state of **1d** and **2d** may partially contribute to the observed rate enhancement. Examination of molecular models suggests that, in analogy with the case of the ^{13}C NMR study, more favorable geometry, both in distance and in orientation, can be attained for the homoallylic interaction between the vacant p orbital at the bridgehead position and the p orbital of the distorted bridgehead double bond with decrease in the size (*n*) of the bicyclo[*n*.2.2] framework. Thus, it may be concluded that the highly strained bridgehead alkenes, especially bicyclo[4.2.2]-decene system, show remarkable homoallylic type α,γ-interaction both in the ground state and in the transition state (carbonium ion).

Experimental

All the melting and boiling points are uncorrected. IR spectra were recorded on a JASCO IR-G spectrometer. Mass spectra were taken by using a Hitachi RMU-6E spectrometer. ^1H NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer and ^{13}C NMR spectra were on a JEOL JNM-FX-60S spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph (10% FFAP or 5% SE-30 column) and preparative GLC separation was undertaken on a Varian Aerograph 920 gas chromatograph. The spectral and analytical data for the bridgehead alkenes **1a**—**3a**, **1b**—**3b**, **1c**—**3c**, and **1d**—**3d** and those for the cyclopropylcarbinyl type tricyclic compounds **7b**, **8b**, **7c**, and **8c** were listed in Table 5.

Preparation of [n.*2.2*]*Propellanecarboxylic Acids* ***4a***—***6a***. The ring contraction of [*n*.3.2]propellanones[7] were carried out by the usual procedure involving the photochemical Wolff rearrangement.[17] Namely, the condensation of [*n*.3.2]propellanones with ethyl formate using sodium hydride in ether[18] gave the corresponding hydroxymethylene derivatives (IR 1670, 1600, 1520, 1180 cm^{-1}) in 80—87% yields and subsequent diazo transfer with tosyl azide[19] gave the corresponding diazo ketones (IR 2050, 1650 cm^{-1}) in quantitative yield. The crude diazo ketones were dissolved in methanol and the solutions were irradiated in a Pyrex vessel with a 500 W high pressure mercury lamp for 16—20 h. The solvent was removed under reduced pressure and the residue distilled to afford the methyl esters (**4b**—**6b**) of [*n*.2.2]propellanecarboxylic acids **4a**—**6a** in 65—85% yields. GLC analysis showed that **4b**—**6b** were the mixtures of epimers in about 1:2 ratio. **4b**: bp 103—105 °C/10 mmHg; IR 1720, 1165 cm^{-1}; MS *m/e* 194 (M^+); ^1H NMR (CCl_4) δ 1.00—2.72 (m, 14H), 3.04, 3.16 (t, J=8 Hz, 1H), 3.58 (s, 3H). Found: C, 74.17; H, 9.43%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%. **5b**: bp 110—112 °C/5 mmHg; IR 1720, 1165 cm^{-1}; MS *m/e* 208 (M^+); ^1H NMR (CCl_4) δ 1.10—2.55 (m, 16H), 3.02, 3.04 (t, J=8 Hz, 1H), 3.59 (s, 3H). Found: C, 74.77; H, 9.79%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%. **6b**: bp 124—128 °C/8 mmHg; IR 1720, 1165 cm^{-1}; MS *m/e* 222 (M^+); ^1H NMR (CCl_4) δ 1.10—2.56 (m, 18H), 3.08 (t, J=8 Hz, 1H), 3.60 (s, 3H). Found: C, 75.35; H, 10.11%. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97%.

The solutions of the esters **4b**—**6b** and 2 equiv. of potassium hydroxide in methanol were heated at reflux for 3 h. The solvent was concentrated and the residue was diluted with water and washed with ether. The aqueous layer was acidified with 6 mol dm^{-3} hydrochloric acid and extracted with ether. Evaporation of the ether gave **4a**—**6a** (92—93% yield) as colorless viscous oil which solidified on standing. IR 3500—2500, 1690, 1220 cm^{-1}. The treatment of **4a**—**6a** with ethereal diazomethane gave **4b**—**6b** having the similar ratio of epimers to that of the original ester mixtures.[20]

Oxidative Decarboxylation of ***4a***—***6a*** *with Lead Tetraacetate.* The solution of **4a**—**6a**, 1.1 equiv. of lead tetraacetate, and 0.6 equiv. of pyridine in benzene was heated under nitrogen at 80 °C for 1 h. After filtration, the solution was washed successively with dilute hydrochloric acid, sodium hydrogencarbonate solution, and water and then dried over anhydrous sodium sulfate (Na_2SO_4). After evaporation of the solvent, the products were analyzed by GLC and the yields determined: **4a**; **7b** (68%), **9** (5%). **5a**; **2b** (13%), **8b** (60%), **10** (3%). **6a**; **3b** (81%). The products were separated by preparative GLC. **9**: IR 3030 cm^{-1}; MS *m/e* 134 (M^+); ^1H NMR (CCl_4) δ 1.20—2.00 (m, 12H), 6.17 (s, 2H). Found: C, 89.20; H, 10.64%. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51%. **10**: IR 3030 cm^{-1}; MS *m/e* 148 (M^+); ^1H NMR (CCl_4) δ 1.10—2.20 (m, 14H), 6.14 (s, 2H). Found: C, 89.06; H, 10.92%. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88%.

Preparation of ***1b*** *and* ***2b*** *by the Rearrangement of* ***7b*** *and* ***8b*** *in Acetic Acid.* The solution of **7b** and **8b** in acetic acid was stirred under nitrogen at room temperature for 5 and 22 h, respectively, and the progress of the reaction was monitored by GLC. The solution was cooled with ice and carefully neutralized with aqueous sodium hydroxide solution and extracted with ether. The ether extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent followed by distillation afforded **1b** and **2b** in 90 and 97% yields, respectively. Analytical sample of **1b** was obtained by preparative GLC.

Preparation of the Bridgehead Alcohols ***1c***—***3c*** *and* ***7c***—***8c*** *by Lithium Aluminum Hydride Reduction of* ***1b***—***3b*** *and* ***7b***—***8b***. The solution of the acetates **1b**—**3b** and **7b**—**8b** in ether was added dropwise to the suspension of lithium aluminum hydride (1 equiv.) in the same solvent and the mixture was stirred at room temperature for 1 h. Water was added dropwise followed by dilute hydrochloric acid. The organic layer was separated and washed with sodium hydrogencarbonate solution and water and then dried (Na_2SO_4). Evaporation of the solvent gave the alcohols **1c**—**3c** and **7c**—**8c** in 68—80% yields which were purified by preparative GLC.

Preparation of the Bridgehead Chlorides ***1d***—***3d***. To the solution of **1c**—**3c** and 5 equiv. of pyridine in benzene was added 2 equiv. of thionyl chloride (phosphoryl chloride was used in the case of **1c**) and the solution was stirred at room temperature for 2 h. Water was added carefully and the organic layer was washed with dilute hydrochloric acid,

sodium hydrogencarbonate solution, and water. After drying over Na_2SO_4, the solvent was evaporated to give **1d**—**3d** as light brown oil (45—87% yields). Pure samples of **1d**—**3d** were obtained by preparative GLC.

*Preparation of **11b**, **11c**, and **12c** by the Diimide Reduction of **1b**, **1c**, and **2c**.* The solution of **1b**, **1c**, and **2c**, 20 equiv. of 90% hydrazine hydrate, and 0.1 equiv. of copper (II) sulfate in ethanol was stirred at room temperature while air was bubbled through a syringe. The course of the reaction was monitored by GLC and the reaction times required for completion were within 1 h for **1b** and **1c** and 20 h for **2c**. However, the similar reaction of **2b**, **3b**, and **3c** was unsuccessful.[10] The solution was diluted with water and extracted with ether. The ether extract was washed with water and dried (Na_2SO_4). After evaporation of the solvent, the products were purified by passing through a silica-gel column. Yields of the isolated products were 71—79%. **11b**: IR 1720, 1255, 1230 cm^{-1}; MS *m/e* 136 (M^+—AcOH); ^1H NMR (CCl_4) δ 1.32—2.40 (m, s at 1.84). Found: C, 73.45; H, 10.37%. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. **11c**: mp 73—74 °C; IR 3350, 1020 cm^{-1}; MS *m/e* 154 (M^+, trace), 136 (M^+—H_2O); ^1H NMR (CCl_4) δ 1.40—2.30 (m). Found: C, 77.49; H, 11.86%. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76%. **12c**: mp 79—80 °C; IR 3350, 1060, 1050 cm^{-1}; MS *m/e* 150 (M^+—H_2O); ^1H NMR (CCl_4) δ 1.35—2.30 (m). Found: C, 78.50; H, 11.63%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

*Preparation of **12b**.* To the solution of 80 mg of **12c** and 120 mg of 4-dimethylaminopyridine in 2 ml of dichloromethane was added with stirring the solution of 100 mg of acetic anhydride in 0.5 ml of dichloromethane and the solution was stirred at room temperature for 6 h. The solution was diluted with ether and washed successively with dilute hydrochloric acid, sodium hydrogencarbonate solution, and water and dried over Na_2SO_4. Evaporation of the solvent gave **12b** as a clear oil (80% yield). IR 1720, 1240 cm^{-1}; MS *m/e* 150 (M^+—AcOH); ^1H NMR (CCl_4) δ 1.10—2.40 (m, s at 1.84).[22]

*Preparation of the Alkenes **1a** and **2a**.* *(a) By the Vapor Phase Thermolysis of **11b** and **12b**:* The 3% solution of **11b** and **12b** in hexane was passed through a Pyrex column which was heated at 350 °C under nitrogen stream (15 ml/min) and the end of the column was connected to a trap containing powdered potassium carbonate cooled at −78 °C. The trapped solution was filtered and concentrated to give **1a** and **2a** as semisolid in 76—82% yields.

*(b) By the Dehydration of **11c** and **12c**:* The treatment of **11c** and **12c** with thionyl chloride/pyridine in the similar manner to the chlorination of **2c** and **3c** afforded **1a** and **2a** in 74—80% yields.

*Preparation of the Alkene **3a**.* The solution of 900 mg of **3d** and 3.3 g of *t*-butyl alcohol in 30 ml of tetrahydrofuran was heated at reflux with stirring and to this solution was added portionwise 315 mg of lithium cut in small pieces. The mixture was heated for 3 h and then poured into water. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts was washed with saturated sodium chloride solution and dried over Na_2SO_4. Evaporation of the solvent followed by distillation gave **3a** as a colorless oil in 67% yield.

*Preparation of the Bridgehead Chloride **11d**.* 138 mg of the alcohol **11c** was added portionwise to 1.0 g of thionyl chloride and the solution was stirred at room temperature for 1 h. Crashed ice was added followed by water and the mixture was extracted with ether. The extract was washed with sodium hydrogencarbonate solution and water and dried over Na_2SO_4. After evaporation of the solvent, **11d** was purified by sublimation (70 °C/20 mmHg): mp 70—71 °C; IR 850 cm^{-1}; MS *m/e* 172 (M^+, trace), 137 (M^+—HCl); ^1H NMR (CCl_4) δ 1.15—2.60 (m). Found: C, 69.94; H, 9.96%. Calcd for $C_{10}H_{17}Cl$: C, 70.14; H, 9.96%.

*Kinetic Measurements of the Ethanolysis of **1d**—**3d** and **11d**.* The solution (0.1 M) of the chlorides and the internal standard (octadecane or nonadecane) in ethanol containing 10% (v/v) of 2,6-lutidine was set in a constant temperature bath and at appropriate intervals aliquots were removed by a syringe and the decrease of the chlorides was determined by GLC. The products of the ethanolysis were isolated by preparative GLC and the ^1H NMR spectra of them were taken. **1d** gave a single ether which showed a multiplet (2H) at δ 0.52—0.98, a triplet at δ 1.21, and a quartet (2H) at δ 3.48 ppm. **2d** gave two ethers in a ratio of 3:1; the former exhibited a multiplet (2H) at δ 0.37—0.88, a triplet at δ 1.24, and a quartet (2H) at δ 3.52 ppm, and the latter a triplet at δ 1.11, a quartet (2H) at δ 3.28, and a multiplet (1H) at δ 5.36—5.52 ppm. **3d** afforded a single ether which showed a triplet at δ 1.15, a quartet (2H) at δ 3.31, and a broad doublet (1H) at δ 5.54 ppm.

*Preparative Hydrolysis of **1d**—**3d**.* The solution of **1d**—**3d** in 80% aqueous acetone containing 5 equiv. of 2,6-lutidine was stand at room temperature over night. The solvent was concentrated and extracted with ether. The products were identified by the comparison in GLC retention times and IR spectra with those of the authentic samples: **1d**; **7c** (96%). **2d**; **8c** (80%), **2c** (12%). **3d**; **3c** (99%).

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9) The catalytic hydrogenation of **1b—3b** and **1c—3c** at atmospheric pressure of hydrogen using Pd/C or PtO_2 catalyst was also unfruitful.

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