(1.0) became the major product. Small amounts of 3-BA (0.3), 4-BA (0.1), and other unidentified products were detected. No 1 could be detected.

Reaction of Acetanilide with *tert*-Butyl Chloride. To acetanilide (5.4 g, 0.040 mol) and $AlCl_3$ (6.7 g, 0.050 mol) in 80 mL of CS_2 was added portionwise *tert*-butyl chloride (4.1 g, 0.044 mol) in 20 mL of CS_2 during a 1-h period. The mixture was stirred and refluxed for 45 min. The reaction was quenched by pouring into ice (500 g) and then the mixture was extracted with CH_2Cl_2 (100 mL). The extract after drying and solvent evaporation gave 6.6 g of a white solid. GC analysis indicated the presence of the following components (relative amounts): acetanilide (1.0), 3-BA (1.6), 4-BA (0.8), and DBA (0.5). The crude reaction mixture was dissolved in ca. 10 mL of hot benzene. To this solution was added cold hexane. The precipitated solid was filtered off, giving 1.4 g (18% yield) of white plates, mp 97–99 °C. This material was identified as 3-BA (lit.[9] mp 99 °C). The solvent from the filtrate and the residue evaporated was dissolved in hot hexane (20 mL). Cooling produced a white precipitate, which after filtration and recrystallization from ethanol gave 4-BA (1.1 g, 14% yield), mp 171–172 °C (lit.[2] mp 171–172 °C).

X-ray Crystallographic Structure Determination for 2,2-Dimethyl-5-*tert*-butyl-7-acetamidoindanone. The compound crystallized in space group P_{nma}. The cell constants were a = 12.571 (3) Å, b = 7.302 (12) Å, c = 16.910 (3) Å, V = 1552.29 Å^3, and Z = 4. The density was 1.17 g cm^{-3} (calcd) and 1.16 g cm^{-3} (measd). The radiation was Mo Kα with a scan technique of ω–2θ with scan width = 0.8 + 0.035 tan θ deg and max 2θ = 50°. With a cutoff for observed reflections of $3\sigma(F^2)$, there were 1476 measured reflections and 1224 observed reflections. The structure was phased by using MULTAN77 and refined well. The final residuals were R_1 = 0.056, R_2 = 0.074. Positional parameters and the ORTEP drawing are available as supplementary data.

Registry No. 1, 88057-11-8; 2, 88057-12-9; 3, 88057-13-0; 4, 88057-14-1; 3-BA, 38382-35-3; 4-BA, 20330-45-4; DBA, 37055-54-2; pivalyl chloride, 3282-30-2; acetanilide, 103-84-4; *tert*-butyl chloride, 507-20-0.

Supplementary Material Available: Tables listing the positional parameters for and the ORTEP drawing of 2,2-dimethyl-5-*tert*-butyl-7-acetamidoindanone (8 pages). Ordering information is given on any current masthead page.

Acid-Catalyzed Rearrangement of [*m*.*n*.2]Propellanones

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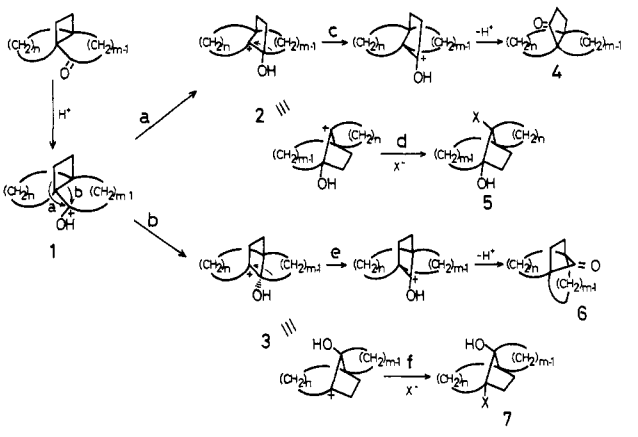
The acid-catalyzed rearrangement of [*m*.*n*.2]propellanones (m = 3–5, n = 3, 4) was studied to ascertain the effect of ring size on the mode of rearrangement. Propellanones **9** and **10**, containing a five-membered cycloalkanone ring, did not rearrange. Propellanones containing a six- or seven-membered cycloalkanone ring (**11**–**14**) rearranged smoothly to cyclopentanones **17a**, **18**, and **19** in a nonnucleophilic medium. In the presence of a nucleophile, the course of the rearrangement depended on whether the third cycloalkane ring contained three, four, or five carbon atoms. Thus propellanones **11** and **14** rearranged to (1*S**,5*R**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecane derivatives **20a,b** and (1*S**,6*R**,7*S**)-tricyclo[5.3.2.0^{1,6}]dodecane derivatives **22a** and **23** by an unusual 1,2 alkyl shift of the central propellane bond followed by nucleophilic attack. The structures of **20a,b**, **22a**, and **23** were established by chemical transformations (Scheme II). The stereochemistry of methyl substituents on the cyclobutane ring of dimethyl[5.3.2]propellanones **15** and **16** influenced the course of rearrangement in the presence of a nucleophile.

As part of a study of the rearrangement of [*m*.*n*.2]propellanes ($m \geq 3$, $n \geq 2$)[1] triggered by strain release of one or two cyclobutane rings, we recently reported a novel acid-catalyzed rearrangement of [4̄.3.2]propellanone (**11**)[1f,2] and [5̄.3.2]propellanone (**14**)[3] to tricyclo[4.3.2.0^{1,5}]undecanes **20a,b** and tricyclo[5.3.2.0^{1,6}]dodecanes **22a** and **23**, respectively.[4]

In general, two modes of migration are available for this rearrangement as shown in Scheme I. One involves a 1,2 alkyl shift of the external cyclobutane bond to afford cation **2** (path a), which undergoes a further 1,2 alkyl shift to give [(m – 1).n.3̄]propellanone **4** (path c)[5] or is trapped by a nucleophile (X^-) to furnish the tricyclic alcohol **5** (path d).[1a] The other mode involves the 1,2 alkyl shift of the central propellane bond (path b) to give either [(m – 1).n.2.1]-

Scheme I



(1) For [*m*.3.2]propellanes ($m \geq 3$): (a) Tobe, Y.; Hayauchi, Y.; Odaira, Y. *J. Org. Chem.* **1981**, *46*, 5219 and reference 3 cited therein. For [*m*.2.2]propellanes ($m \geq 3$): (b) Sakai, Y.; Terashima, K.; Tobe, Y.; Odaira, Y. *Bull. Soc. Chem. Jpn.* **1981**, *54*, 2229 and ref 4 cited therein. (c) Tobe, Y.; Yonezawa, T.; Kakiuchi, K.; Odaira, Y. *Ibid.* **1982**, *55*, 3262. (d) Tobe, Y.; Kishimura, T.; Kakiuchi, K.; Odaira, Y. *J. Org. Chem.* **1983**, *48*, 551. (e) Tobe, Y.; Kakiuchi, K.; Odaira, Y.; Hosaki, T.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 1376. For [*m*.*n*.2]propellalactones ($m \geq 4$, $n \geq 3$): (f) Kakiuchi, K.; Tsugaru, T.; Tobe, Y.; Odaira, Y. *J. Org. Chem.* **1981**, *46*, 4204 and ref 2 cited therein.

(2) Tricyclo[4.3.2.0^{1,6}]undecan-2-one. In the propellane nomenclature the bridge number of the carbonyl-bearing ring is indicated by a bar; in all compounds in this paper the carbonyl group is adjacent to the 0 bridge.

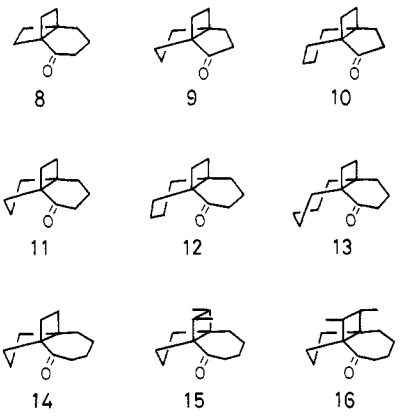
(3) Tricyclo[5.3.2.0^{1,7}]dodecan-2-one. Kunai, A.; Omori, T.; Miyata, T.; Kimura, K.; Odaira, Y. *Tetrahedron Lett.* **1974**, 2517.

(4) Kakiuchi, K.; Hato, Y.; Tobe, Y.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 6.

(5) (a) Cargill, R. L.; Jackson, T. E.; Peet, N. P.; Pond, D. M. *Acc. Chem. Res.* **1974**, *7*, 106. (b) Cargill, R. L.; Bryson, T. A.; Krueger, L. M.; Kempf, J. V.; McKenzie, T. C.; Bordner, J. *J. Org. Chem.* **1976**, *41*, 4096. (c) Cargill, R. L.; Bushey, D. F.; Dalton, J. R.; Prasad, R. S.; Dyer, R. D.; Bordner, J. *Ibid.* **1981**, *46*, 3389. (d) Smith, A. B., III; Jerris, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 194.

0022-3263/84/1949-0659$01.50/0

Chart I

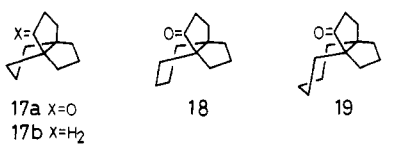


paddlanone **6** by an additional 1,2 alkyl shift (path e) or the tricyclic alcohol **7** by trapping with a nucleophile (path f). There are several reports of the path a mode of migration, for example, the acid-catalyzed rearrangement of [4.3̄.2]-, [4̄.3.2]-, and [4̄.4.2]propellanone derivatives in nonnucleophilic media.[5a-c] On the other hand, the path b mode of migration has been reported only recently. Eaton gave an example of this mode in the acid-catalyzed rearrangement of highly strained [4̄.2.2]propellanone (**8**,[6] Chart I) in the presence of several nucleophiles. Eaton's and our findings on the path b mode of migration suggest that the migratory modes of [*m.n.*2]propellanones might be influenced by the sizes of their rings as well as by the presence or absence of a nucleophile.

In this paper we describe a systematic investigation of the acid-catalyzed rearrangement of [*m.n.*2]propellanones **9–14** to examine the generality of the path b rearrangement to tricyclic ring systems and to elucidate the effects of propellanone ring size on the migratory mode. Since **9–14** are constituted of a cyclobutane, a five- to seven-membered cycloalkanone, and a five- to seven-membered cycloalkane (which we refer to as the third ring), the effect of the sizes of the latter two rings on the mode of migration could be determined. In addition, the acid-catalyzed rearrangement of dimethyl[5̄.3.2]propellanones **15** and **16**[7] was studied to determine the effect of methyl substitution on the cyclobutane ring on the mode of migration.

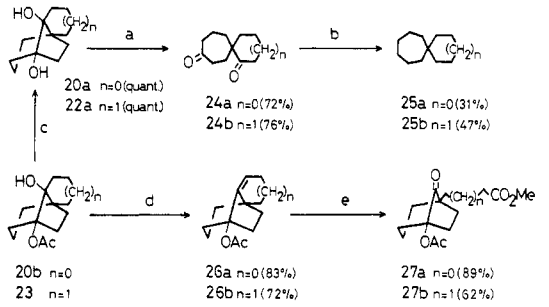
Results

To study the effect of third ring size, we investigated the acid-catalyzed rearrangement of [4̄.3.2]propellanone (**11**),[2] [4̄.4.2]propellanone (**12**),[8] and [5.4̄.2]propellanone (**13**),[9] which have five-, six-, and seven-membered third rings, respectively. Treatment of **11** or **12** with *p*-toluenesulfonic acid (TsOH) in benzene at reflux gave [3̄.3.3]propellanone (**17a**) or [4.3̄.3]propellanone (**18**) as the



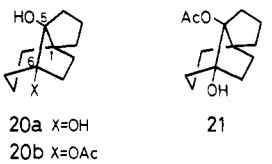
sole product (80% and 90% yields) in accord with the results of Cargill et al.[8] Moreover, similar treatment of **13** gave [5.3̄.3]propellanone (**19**) in quantitative yield. The structure assignments of **17a**, **18**, and **19** are based on spectroscopic data, particularly the IR carbonyl absorption at 1730–1735 cm^{-1} due to a cyclopentanone ring. The structure of **17a** was confirmed by the ^{13}C NMR spectrum of the hydrocarbon **17b**[10] derived from it by Wolff–Kishner reduction. Thus the rearrangement of propellanones **11–13** in a nonnucleophilic medium follows path a and path c to afford [*m*.3.3]propellanones (*m* = 3–5) regardless of the size of the third ring.

Scheme II[a]

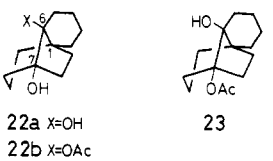


[a] (a) $Pb(OAc)_4$, PhH; (b) (1) $HS(CH_2)_2SH$, $BF_3 \cdot OEt_2$, (2) Raney Ni (W-4), EtOH; (c) $LiAlH_4$, Et_2O; (d) $SOCl_2$/Py, CH_2Cl_2; (e) (1) OsO_4, Py, (2) $Pb(OAc)_4$, PhH, (3) Br_2-H_2O, (4) CH_2N_2, Et_2O.

On the other hand, in the presence of a nucleophile, the rearrangement of **11–13** is influenced by the size of the third ring. Reaction of **11** with H_2SO_4 in aqueous THF afforded (1*S**,5*R**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecane-5,6-diol (**20a**) in 83% yield along with a trace of **17a**. Similarly,



treatment of **11** with TsOH in acetic acid gave the hydroxy acetate **20b** (68%) together with **17a** (15%). However, reaction of **12**, which has a six-membered third ring, with H_2SO_4 in aqueous THF gave **18** as the major product (71%) along with a small amount (9%) of (1*S**,6*R**,7*S**)-tricyclo[5.3.2.0^{1,6}]dodecane-6,7-diol (**22a**)



and a trace of two unidentified products, A and B. With TsOH in acetic acid **12** again afforded mainly **18** (61%) together with **22b** and the unidentified A and B (~20%). Propellanone **13**, with a seven-membered third ring, gave only **19** (72% with H_2SO_4 in aqueous THF and 94% with TsOH in acetic acid) via path a and path c and no diol or hydroxy acetate.

The structures of **20a** and **20b** were elucidated on the basis of spectroscopic data and the following chemical transformations. Lead tetraacetate oxidation of **20a** to spiro[4.6]undecane-1,8-dione (**24a**) and reduction of the thioketal of **24a** gave spiro[4.6]undecane (**25a**), which was identical with an authentic sample. Since $LiAlH_4$ reduc-

(6) Tricyclo[4.2.2.0^{1,6}]decan-2-one. Eaton, P. E.; Jobe, P. G.; Nyi, K. *J. Am. Chem. Soc.* **1980**, *102*, 6638.

(7) (1*S**,7*S**,11*S**,12*S**)-11,12-dimethyltricyclo[5.3.2.0^{1,7}]dodecan-2-one and (1*S**,7*S**,11*R**,12*R**)-11,12-dimethyltricyclo[5.3.2.0^{1,7}]dodecan-2-one, respectively.

(8) Tricyclo[4.4.2.0^{1,6}]dodecan-2-one. Peet, N. P.; Cargill, R. L.; Bushey, D. F. *J. Org. Chem.* **1973**, *38*, 1218.

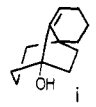
(9) Tricyclo[5.4.2.0^{1,7}]tridecan-8-one.

(10) (a) Cargill, R. L.; Dalton, J. R.; O'Connor, S.; Michels, D. G. *Tetrahedron Lett.* **1978**, 4465. (b) Inamoto, Y.; Aigami, K.; Fujikura, Y.; Takaishi, N.; Tsuchihashi, K. *J. Org. Chem.* **1979**, *44*, 854.

tion of hydroxy acetate **20b** afforded diol **20a**, the carbon skeleton of **20a** and **20b** was established as a 5,6-disubstituted tricyclo[4.3.2.0^{1,5}]undecane. To determine the position of the acetoxy group, **20b** was dehydrated with thionyl chloride–pyridine followed by (1) oxidation of the olefin **26a** with osmium tetraoxide, (2) oxidative cleavage of the vicinal diol with lead tetraacetate, (3) oxidation with Br_2–H_2O, and (4) treatment with ethereal diazomethane, as shown in Scheme II. The resulting keto ester **27a** showed an IR absorption at 1760 cm^{-1}, which is characteristic of a bicyclo[3.2.1]octan-8-one,[11] and we therefore conclude that the acetoxy group is located at C-6 (**20b**) rather than at C-5 (**21**). Finally, the (1*S**,5*R**,6*S**) stereochemistry of **20a** and **20b** was presumed on the basis of the greater thermodynamic stability (5–6 kcal/mol) of (1*S**,5*R**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecane than that of the 1*S**,5*S**,6*R** isomer.[12] We therefore conclude that the formation of **20a** and **20b** involves a 1,2 alkyl shift of the central bond (path b) followed by attack of the nucleophile at the bridgehead cation (path f); a 1,2 alkyl shift of the external bond (path a) followed by attack of acetate ion (path d) would lead to **21**.

The structure of diol **22a** was established by its identity with the diol obtained from the acid-catalyzed rearrangement of [$\bar{5}$.3.2]propellanone (**14**) with H_2SO_4 in aqueous THF (see below). Since hydroxy acetate **22b** gave diol **22a** on reduction with $LiAlH_4$ but was different from the 6-hydroxy 7-acetate **23** derived from treatment of **14** with TsOH in acetic acid (see below), the structure of **22b** was shown to be 7-hydroxytricyclo[5.3.2.0^{1,6}]dodecan-6-yl acetate. The stereochemistry of C-6 in **22a** and **22b** is assumed to be 1*S**,6*R**,7*S** on the basis of mechanistic considerations, i.e., back-side attack of a nucleophile on the developing p orbital.[5c] It is evident that **22a** and **22b**, like **18**, are formed through a 1,2 alkyl shift of the external cyclobutane bond (path a).

Although the structure of A has not been determined, spectral data and the elemental analysis indicate that it is a tricyclic tertiary alcohol with a trisubstituted double bond. It is different from i, which could be formed from



i

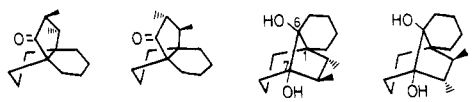
12 by external bond migration (path a) followed by deprotonation and which was prepared by $LiAlH_4$ reduction of **26b**.

To examine the effect of the size of the cycloalkanone ring on the mode of migration, we studied the cyclopentanone derivatives **9**[13] and **10**[14] and the cycloheptanone derivative **14**, which have five- or six-membered third rings. Propellanones **9** and **10** did not undergo acid-catalyzed rearrangement, even in the presence of a nucleophile (H_2O–H_2SO_4–THF), despite the fact that the corresponding tosylates readily underwent rearrangement involving the external bond in buffered solvolyses.[1a]

Rearrangement of **14** occurred smoothly in the absence of a nucleophile to give [4.$\bar{3}$.3]propellanone (**18**, 71%), formed by path a–c. Reaction of **14** with H_2SO_4 in aqueous THF followed a different route to give **22a** as the major product (88%) along with a trace of **18**. Moreover, reaction of **14** with TsOH in acetic acid gave (1*S**,6*R**,7*S**)-6-hydroxytricyclo[5.3.2.0^{1,6}]dodecan-7-yl acetate (**23**, 80%) with a small amount (2%) of **18**.

The structures of **22a** and **23** were established by the same sequences used for **20a** and **20b** (Scheme II). The spiro[5.6]dodecane (**25b**) was identical with an authentic sample[15] and was different from an authentic sample of spiro[4.7]dodecane, which could have been formed from **14** by path a–d. Keto ester **27b**, like **27a**, had an IR absorption at 1760 cm^{-1}, showing that the acetoxy group of **23** is located at C-7. These results reveal that the formation of **22a** and **23** involves the 1,2 alkyl shift of the central bond (path b) followed by path f, analogous to the rearrangement of **11**.

Finally, the acid-catalyzed rearrangement of the dimethyl[$\bar{5}$.3.2]propellanone **15** and **16** were investigated to examine the effects of methyl groups on the cyclobutane ring. It was established that **15** and **16** have cis-syn-trans and cis-anti-trans structures, respectively, from their ^{1}H NMR spectra by using the shift reagent Eu(dpm)$_3$[16] and from comparison of **16** with an authentic sample prepared by ring enlargement of *cis-anti-trans*-dimethyl[$\bar{4}$.3.2]-propellanone.[8] The acid-catalyzed rearrangement of **15** and **16** in TsOH–benzene proceeded smoothly via path a–c to give the corresponding dimethyl[4.$\bar{3}$.3]propellanones **28** (96%) and **29** (83%), respectively. Since the basic skeleton of **15** and **16** is the same as **14**, it was expected that their rearrangement in nucleophilic media should also take place through the central bond shift (path b). Indeed, the cis-syn-trans isomer **15** rearranged in H_2SO_4–aqueous THF via path b–f to afford (1*S**,6*R**,7*S**,11*R**,12*S**)-11,12-dimethyltricyclo[5.3.2.0^{1,6}]dodecane-6,7-diol (**30**, 62%) with a small amount of **28** (10%). On the other hand, under the same conditions the cis-anti-trans isomer **16** was converted largely into **29** (78%), with formation of only a trace of the path b–f diol **31**.[17]



28 29 30 31

The results of the acid-catalyzed rearrangement of propellanones **9**–**16**, as well as that of [$\bar{4}$.2.2]propellanone (**8**),[6] are summarized in Table I.

Discussion

As shown in Table I (entries 3–6), the size of the third ring affects the migratory modes of the acid-catalyzed rearrangement of [*m.n.*2]propellanones. The [$\bar{4}$.2.2]- and [$\bar{4}$.3.2]propellanones (**8** and **11**), with a cyclobutane or cyclopentane third ring, rearrange predominantly by the central bond shift (path b) in the presence of a nucleophile. On the other hand, [$\bar{4}$.4.2]- and [$\bar{5}$.4.2]propellanones (**12** and **13**), with a cyclohexane or cycloheptane third ring, give only the products derived from an external bond shift (path a) under the same conditions. It is therefore deduced that the migratory modes of the acid-catalyzed rearrangement of [*m.n.*2]propellanones depend on the degree of strain in the central propellane bond. In the highly

(11) Cope, A. C.; Grisar, J. M.; Peterson, P. E. *J. Am. Chem. Soc.* **1960**, *82*, 1218.
(12) Ōsawa, E.; Aigami, K.; Takaishi, N.; Inamoto, Y.; Fujikura, Y.; Majerski, Z.; Schleyer, P. v. R.; Engeler, E. M.; Farcasiu, M. *J. Am. Chem. Soc.* **1977**, *99*, 5361.
(13) Tricyclo[3.3.2.0^{1,5}]decan-2-one. (a) Cargill, R. L.; Damewood, J. R.; Cooper, M. M. *J. Am. Chem. Soc.* **1966**, *88*, 1330. (b) Tobe, Y.; Doi, A.; Kimura, K.; Odaira, Y. *Bull. Soc. Chem. Jpn.* **1979**, *52*, 639.
(14) Tricyclo[4.3.2.0^{1,6}]undecan-7-one. Kunai, A.; Yorihiro, K.; Hirata, T.; Odaira, Y. *Tetrahedron* **1973**, *29*, 1679.
(15) Dixon, J. A.; Naro, P. A. *J. Org. Chem.* **1960**, *25*, 2904.
(16) Cockerill, A. F.; Rackham, D. M. *Tetrahedron Lett.* **1970**, 5149. The *S* values of C-11 and C-12 methyl protons in the LIS NMR spectra of **15** or **16** were 9.76 and 3.06 or 4.86 and 2.87.
(17) The structure of **31** could not be determined but was presumed to be a diol corresponding to **30** on the basis of IR and mass spectra and mechanistic consideration of the rearrangement of **16**.

Table I. Acid-Catalyzed Rearrangement of [m.n.2]Propellanones

entry	[m.n.2]propellanone compd	ring size: cycloalkanone	ring size: third ring	nucleophile	product (%): external bond shift path a–c	product (%): central bond shift path b–f
1	[3.3.2]9	5	5	H_2O[a]		
2	[4.3.2]10	5	6	H_2O[a]		
3	[4.2.2]8[b]	6	4	none[a]		
				H_2O		100
4	[4.3.2]11	6	5	none	80	
				H_2O	trace	83
				AcOH	15	68
5	[4.4.2]12	6	6	none[c]	90	
				H_2O[d]	71	
				AcOH[e]	61	
6	[5.4.2]13	6	7	none	99	
				H_2O	72	
				AcOH	94	
7	[5.3.2]14	7	5	none	71	
				H_2O	trace	88
				AcOH	2	80
8	*cis-syn-trans*-[5.3.2]15	7	5	none	96	
				H_2O	10	62
9	*cis-anti-trans*-[5.3.2]16	7	5	none	83	
				H_2O	78	trace

[a] No reaction. [b] Reference 6. [c] See also ref 8. [d] The products included **22a** (path d, 9%) and unidentified compounds A and B (trace). [e] The products included **22b** (path d, 6%) and unidentified compounds A and B (~20%).

strained **8** and the moderately strained **11**, the migration of the central bond may be kinetically more favorable than that of the external bond. It is known that the central bond of highly strained small ring propellanes has extensive p orbital character,[18] and, consequently, participation of the central bond in the adjacent carbonium ion center is to be expected.[1b-e,18a] However, rearrangement of **11** in the absence of a nucleophile gives [3.3.3]propellanone **17a** by path a–c under thermodynamic control, since the formation of a highly strained paddlanone, **6**, is unlikely.

In contrast to **8** and **11**, **12**, even in the presence of a nucleophile, gives only small amounts of the products **22a** and **22b** derived from reaction with the nucleophile (path d), and **13** forms no products by this path. These facts suggest that the further Wagner–Meerwein shift (path c) of the cation intermediate **2** takes place more rapidly than the attack of a nucleophile on cation **2** (path d). Although the real reason is not yet clear, it is reasonable to consider that the relative thermodynamic stabilities of the propellanones **4** (m = 4, n = 3–5) and the tricyclic compounds **5** may account to a considerable extent for the above difference in product distribution. The propellanones **4** (m = 4, n = 4, 5) may be thermodynamically more stable than the corresponding tricyclic compounds **5** (m = 4, n = 4, 5) in view of the greater thermodynamic stability of [3.3.3]propellane (**17b**) over tricyclo[4.3.2.0^{1,5}]undecane.[12]

The results in Table I (entries 1, 2, 4, 5, and 7) demonstrate that the ring size of the cycloalkanone moiety greatly affects the acid-catalyzed rearrangement of [m.n.2]propellanones. The acid-catalyzed rearrangement was not observed with the cyclopentanone derivatives **9** and **10** while the cyclohexanone derivatives **11** and **12** underwent rearrangement readily. Moreover, the rearrangement of **14** occurred more readily than that of **11** (see Experimental Section). Fetizon et al. have pointed out that in the acid-catalyzed rearrangement of cyclobutylcarbinyl ketones the dihedral angle between the carbonyl axis and the migratory bond has an important influence on reactivity.[19] We therefore infer that the ring size effect of the cycloalkanone moieties in our propellanones can be attributed to their conformational flexibility for achieving maximum interaction of the p orbital of the cycloalkyl cation **1** with the central or external cyclobutane bond. Thus while the cyclohexanone and cycloheptanone derivatives **11**, **12**, and **14** undergo rearrangement readily because of the flexibility of the cycloalkanone moiety, **9** and **10** are unreactive because of the rigidity of the cyclopentanone ring.

Entries 8 and 9 of Table I show that the stereochemistry of methyl substituents on the cyclobutane ring also affects the migratory modes of the rearrangement. The cis-anti-trans ketone **16** rearranges predominantly through an external bond shift (path a–c), while the rearrangement of the cis-syn-trans isomer **15** proceeds via path b–f as does that of the unsubstituted propellanone **14**. This difference is probably due to the difference in thermodynamic stability of the two cation intermediates **32** and **33**. In **33**

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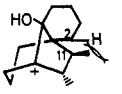

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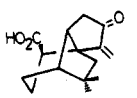
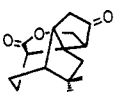
there may be considerable steric interaction between a C-2 hydrogen and the exo C-11 methyl group, so that **16** is forced to rearrange via path a–c under thermodynamic control.

The rearrangement of propellanones such as **11** and **14**, which are readily available by the photocycloaddition of ethylene to α,β-unsaturated ketones, offer an efficient route to the synthesis of novel tricyclic systems. The tricycloundecane derivatives **20a,b** have the same skeleton as terrecyclic acid (**34**)[20] and the final precursor of quadrone



34



35

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(19) Duc, D. K. M.; Fetizon, M.; Kone, M. *Tetrahedron* **1978**, *34*, 3513.

(35),[21] which are of interest because of their unusual structures and biological activity. The synthesis of compounds related to the sesquiterpenes by way of this rearrangement is being undertaken, with further investigation of the rearrangement mechanism.

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on a Hitachi 260-10 spectrometer as liquid films unless otherwise stated. ^1H NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer in CCl_4 unless otherwise stated, and ^{13}C NMR spectra were taken on a JEOL JNM-FX-60S spectrometer in $CDCl_3$ with Me_4Si as an internal standard. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph, and preparative GLC was conducted on a Varian Aerograph 920 gas chromatograph with a 10% FFAP column.

Materials. [3.3.2]Propellanone (**9**),[13b] [4.3.2]propellanone (**10**),[14] [4.3.2]propellanone (**11**),[1f] [4.4.2]propellanone (**12**),[1f,8] and [5.3.2]propellanone (**14**)[3] were prepared as described previously. [5.4.2]Propellanone (**13**) was prepared by the ring enlargement of [5.3.2]propellanone[13b] (overall yield 31%) according to the reported method for the preparation of **12**.[1f] **13**: IR 1690 cm^{-1}; MS, m/e (relative intensity) 192 (M^+, 25), 164 (100); ^1H NMR δ 0.90–2.60 (m); semicarbazone, mp 225–227 °C. Anal. Calcd for $C_{14}H_{23}ON_3$: C, 67.44; H, 9.23; N, 16.86. Found: C, 67.43; H, 9.30; N, 16.85.

Dimethyl[5.3.2]propellanones 15 and 16. A solution of 5.00 g (33.3 mmol) of bicyclo[5.3.0]dec-1(7)-en-8-one[3] and ca. 20 mL of *cis*-2-butene in methylene chloride (240 mL) was irradiated through a Pyrex filter for 1.5 h at −70 °C. Disappearance of the enone was monitored by GLC. The solution was warmed to room temperature, and the solvent was removed in vacuo. The residue was distilled under reduced pressure to give 5.62 g of a mixture containing **15** (49%), **16** (35%), and other adducts (16%) as determined by GLC. These products were separated by column chromatography on silica gel and purified by preparative GLC.

15: IR 1690 cm^{-1}; MS, m/e (relative intensity) 206 (M^+, 3), 151 (100); ^1H NMR δ 0.88 (d, 3 H), 1.06 (d, 3 H), 1.90–2.00 (m, 14 H), 2.24–2.56 (m, 2 H). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.16; H, 10.97.

16: IR 1690 cm^{-1}; MS, m/e (relative intensity) 206 (M^+, 73), 150 (100); ^1H NMR δ 0.84 (d, 3 H), 0.90 (d, 3 H), 1.08–2.60 (m, 16 H). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.23; H, 10.98. **16** was also obtained from *cis-anti-trans*-dimethyl[4.3.2]propellanone by ring enlargement similar to that of **13** in a 26% overall yield.

General Procedure of Acid-Catalyzed Reaction of Propellanones 9–16. In a Nonnucleophilic Medium. A solution of the ketone and a equal or small excess amount of *p*-toluenesulfonic acid monohydrate ($TsOH\cdot H_2O$) in benzene was heated at reflux. The progress of the reaction was monitored by GLC. The cooled reaction solution was washed with saturated $NaHCO_3$ solution, and the aqueous solution was extracted with ether. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to leave the crude products.

In a Nucleophilic Medium. (A) A solution of 500 mg of the ketone, 0.5 mL of concentrated sulfuric acid, and 0.5 mL of water in 5 mL of tetrahydrofuran was heated at 50 °C unless otherwise stated. The progress of the reaction was monitored by GLC. After evaporation of THF in vacuo, the reaction mixture was diluted with water and extracted with chloroform. The organic layer was washed with water, dried ($MgSO_4$), and concentrated in vacuo to leave the crude products. (B) A solution of 500 mg of the ketone and a catalytic amount of $TsOH\cdot H_2O$ in 10 mL of acetic acid was heated at 50 °C. The progress of the reaction was monitored by GLC. The cooled reaction solution was neutralized with saturated $NaHCO_3$ solution, and the mixture was extracted with methylene chloride. The organic layer was washed with water, dried ($MgSO_4$), and concentrated in vacuo to leave the crude products. The products were separated by column chromatography on silica gel and purified by preparative GLC.

[3.3.3]Propellanone (17a).[10a] The reaction of 239 mg (1.46 mmol) of **11** and $TsOH\cdot H_2O$ (264 mg) in 10 mL of benzene for 2 h gave **7a**: 192 mg (80%); mp 54–55 °C; IR (KBr) 1735 cm^{-1}; MS, m/e (relative intensity) 164 (M^+, 58), 136 (61), 108 (89), 107 (100), 80 (92), 79 (80); ^1H NMR δ 1.12–2.00 (m, 14 H), 2.23 (t, 2 H).

[4.3.3]Propellanone (18).[8] The reaction of 290 mg (1.63 mmol) of **12** and $TsOH\cdot H_2O$ (571 mg) in 20 mL of benzene for 1 h gave **18**: 262 mg (90%); IR (KBr) 1735 cm^{-1}; MS, m/e (relative intensity) 178 (M^+, 84), 136 (57), 123 (69), 122 (90), 121 (100), 79 (58). The reaction of 377 mg (2.12 mmol) of **14** and $TsOH\cdot H_2O$ (400 mg) in 20 mL of benzene for 4 h gave 267 mg (71%) of **18**.

[5.3.2]Propellanone (19). The reaction of 157 mg (0.82 mmol) of **13** and $TsOH\cdot H_2O$ (181 mg) in 25 mL of benzene for 2 h gave **19**: 155 mg (99%); IR 1730 cm^{-1}; MS, m/e (relative intensity) 192 (M^+, 33), 135 (57), 123 (100), 104 (35); ^1H NMR δ 0.92–2.04 (m, 18 H), 2.24 (t, 2 H). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.85; H, 10.48. The reaction of 97 mg (0.51 mmol) or 224 mg (1.17 mmol) of **13** by method A or B for 12–24 h gave 70 mg (72%) or 211 mg (94%) of **19**.

(1*S,5*R**,6*S**)-Tricyclo[4.3.2.0^{1,5}]undecane-5,6-diol (20a).** The reaction of 965 mg (5.88 mmol) of **11** by method A for 96 h gave a trace of **17a** and the diol **20a**: 727 mg (83%); mp 120–122 °C; IR (KBr) 3380, 1150, 1090 cm^{-1}; MS, m/e (relative intensity) 182 (M^+, 34), 164 (56), 97 (100); ^1H NMR ($CDCl_3$) δ 1.12–2.48 (m); ^{13}C NMR δ 87.87 (s), 81.09 (s), 52.03 (s), 34.52 (t), 34.13 (t), 33.77 (t), 31.82 (t), 39.87 (t), 28.96 (t), 20.46 (t), 19.87 (t). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.13; H, 9.92.

(1*S,5*R**,6*S**)-5-Hydroxytricyclo[4.3.2.0^{1,5}]undecan-6-yl Acetate (20b).** The reaction of 397 mg (2.42 mmol) of **11** by method B for 144 h gave 60 mg (15%) of **17a** and the hydroxy acetate **20b**: 364 mg (68%); IR 3450, 1735, 1710,[22] 1280, 1250 cm^{-1}; MS, m/e (relative intensity) 224 (M^+, trace), 164 (98), 136 (100), 118 (58); ^1H NMR δ 1.06–2.16 (m, 18 H, contains s at 1.96), 2.28–2.60 (m, 1 H), 4.08 (s, 1 H); ^{13}C NMR δ 172.22 (s), 92.81 (s), 85.96 (s), 53.82 (s), 34.54 (t), 34.25 (t), 31.90 (t), 30.14 (t, 2 C), 29.96 (t), 21.87 (q), 20.65 (t), 20.30 (t). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.68; H, 9.28.

(1*S,6*R**,7*S**)-Tricyclo[5.3.2.0^{1,6}]dodecane-6,7-diol (22a).** The reaction of 527 mg (2.96 mmol) of **14** by method A at room temperature for 20 h gave a trace of **18** and the diol **22a**: 510 mg (88%); mp 85–86 °C; IR (KBr) 3330, 1180, 1115 cm^{-1}; MS, m/e (relative intensity) 196 (M^+, 56), 178 (100, $M^+ - H_2O$), 149 (45), 109 (76); ^1H NMR ($CDCl_3$) δ 0.72–2.28 (m, 18 H), 2.39 (s, 2 H); ^{13}C NMR δ 80.90 (s), 77.90 (s), 42.74 (s), 34.21 (t), 34.04 (t), 31.77 (t), 30.92 (t), 29.18 (t), 25.80 (t), 21.43 (t), 21.02 (t), 19.16 (t). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.17. Found: C, 73.39; H, 10.35. The reaction of 231 mg (1.30 mmol) of **12** by method A for 48 h gave **18** (164 mg, 71%), unidentified products A and B (<1%), and the diol **22a**, 22 mg (9%).

(1*S,6*R**,7*S**)-7-Hydroxytricyclo[5.3.2.0^{1,6}]dodecan-6-yl Acetate (22b).** The reaction of 226 mg (1.17 mmol) of **12** by method B for 48 h gave **18** (137 mg, 61%), the two unidentified products A (17%) and B (~3%), and the hydroxy acetate **22b**: 18 mg (6%); mp 96–97 °C; IR (KBr) 3450, 1710,[22] 1290, 1255 cm^{-1}; MS, m/e (relative intensity) 238 (M^+, 7), 178 (100, M^+ – AcOH), 149 (39), 136 (49); ^1H NMR δ 0.80–2.56 (m, 21 H, contains s at 2.08), 4.37 (s, 1 H). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.51; H, 9.28.

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(22) The splitting or high-frequency shift of the carbonyl absorption of the acetoxyl group is presumably due to the intramolecular hydrogen bonding with the vicinal hydroxyl group.

Unidentified product A: IR 3400, 3030, 1060 cm^{-1}; MS, *m/e* (relative intensity) 178 (M^+, 60), 149 (100), 135 (33), 107 (34); ^1H NMR δ 0.92–2.80 (m, 17 H), 4.96 (t, 1 H). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.49; H, 10.31.

(1*S,6*R**,7*S**)-6-Hydroxytricyclo[5.3.2.0^{1,6}]dodecan-7-yl Acetate (23).** The reaction of 825 mg (4.63 mmol) of **14** by method B for 15 h gave **18** (17 mg, 2%) and the hydroxy acetate **23**: 880 mg (80%); IR 3450, 1735, 1710,[22] 1280, 1260 cm^{-1}; MS, *m/e* (relative intensity) 238 (M^+, 9), 178 (100, M^+ – AcOH), 149 (72); ^1H NMR δ 0.68–1.86 (m, 17 H), 1.94 (s, 3 H), 2.40–2.60 (m, 1 H), 3.88 (s, 1 H); ^{13}C NMR δ 172.41 (s), 93.59 (s), 76.72 (s), 44.33 (s), 34.00 (t), 31.70 (t), 30.73 (t), 29.84 (t, 2 C), 25.98 (t), 21.79 (q), 21.23 (t), 20.65 (t), 19.47 (t). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.75; H, 9.48.

(1*S,6*S**,8*S**,9*S**)-8,9-Dimethyl[4.3.3]propellanone (28).** The reaction of 106 mg (0.51 mmol) of **15** and $TsOH\cdot H_2O$ (115 mg) in 20 mL of benzene for 5 h gave **28**: 102 mg (96%); IR 1735 cm^{-1}; MS, *m/e* (relative intensity) 206 (M^+, 55), 150 (43), 122 (100); ^1H NMR δ 1.01 (d, 3 H), 1.11 (d, 3 H), 1.20–2.20 (m, 16 H). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.23; H, 10.90.

(1*S,6*S**,8*R**,9*R**)-8,9-Dimethyl[4.3.3]propellanone (29).** The reaction of 60 mg (0.29 mmol) of **16** and $TsOH\cdot H_2O$ (67 mg) in 15 mL of benzene for 20 h gave **29**: 50 mg (83%); IR 1735 cm^{-1}; MS, *m/e* (relative intensity) 206 (M^+, 52), 150 (32), 122 (100); ^1H NMR δ 1.01 (d, 3 H), 1.09 (d, 3 H), 1.16–2.16 (m, 16 H). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.14; H, 10.97. The reaction of 257 mg (1.25 mmol) of **16** by method A for 94 h gave **29** (201 mg, 78%) and a trace of the diol **31**:[17] IR 3370, 1180, 1000 cm^{-1}; MS, *m/e* (relative intensity) 224 (M^+, 44), 206 (93), 150 (76), 149 (100), 122 (56).

(1*S,6*R**,7*S**,11*R**,12*S**)-11,12-Dimethyltricyclo-[5.3.2.0^{1,6}]dodecane-6,7-diol (30).** The reaction of 220 mg (1.08 mmol) of **15** by method A for 16 h gave **28** (22 mg, 10%) and the diol **30**: 148 mg (62%); mp 133 °C; IR (KBr) 3450, 3360, 1190, 1000 cm^{-1}; MS, *m/e* (relative intensity) 224 (M^+, 59), 206 (100, $M^+ - H_2O$), 191 (76), 149 (69), 111 (68); ^1H NMR ($CDCl_3$) δ 0.88 (d, 3 H), 1.06 (d, 3 H), 1.18–2.26 (m, 18 H); ^{13}C NMR δ 82.06 (s), 78.97 (s), 44.11 (s), 43.40 (d), 39.40 (d), 35.21 (t), 29.18 (t), 28.55 (t), 28.36 (t), 21.33 (t), 20.89 (t), 18.48 (t), 16.33 (q), 11.97 (q). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.62; H, 10.66.

Acid-Catalyzed Reactions of [3.3.2]Propellanone (9) and [4.3.2]Propellanone (10). The reaction of 666 mg (4.44 mmol) of **9** by method A for 180 h gave only polymeric materials, and 200 mg (30%) of **9** was recovered. The reaction of 705 mg (4.30 mmol) of **10** by method A for 195 h gave only polymeric materials, and 200 mg (28%) of **10** was recovered.

Lithium Aluminum Hydride Reduction of 20b to 20a. To a stirred suspension of 38 mg (1.0 mmol) of lithium aluminum hydride in 7 mL of dry ether was added dropwise a solution of 186 mg (0.83 mmol) of **20b** in 7 mL of dry ether, and the mixture was stirred at room temperature for 1 h. Water was added carefully, and 10% HCl was subsequently added to dissolve the white precipitate. The organic layer was separated, and the aqueous solution was extracted with ether. The combined extracts were washed with saturated $NaHCO_3$ solution and brine and dried ($MgSO_4$). The solvent was evaporated in vacuo to give 151 mg of a diol (quantitative) which was purified by preparative GLC. The melting point, IR spectrum, and GLC retention time of the diol were identical with those of **20a**.

Lithium Aluminum Hydride Reduction of 22b to 22a. Lithium aluminum hydride reduction of 87 mg (0.37 mmol) of **22b** was carried out as described above to give 70 mg (98%) of a diol whose melting point, IR and mass spectra, and GLC retention time were identical with those of **22a**.

Lithium Aluminum Hydride Reduction of 23 to 22a. An 87-mg (0.37 mmol) sample of **23** was reduced by lithium aluminum hydride as described above to afford 72 mg of a diol (quantitative) whose melting point, IR spectrum, and GLC retention time were identical with those of **22a**.

[3.3.3]Propellane (17b). A solution of 624 mg (3.80 mmol) of **17a**, 0.8 g of KOH, and 0.7 mL of 80% hydrazine hydrate in 7 mL of diethylene glycol was refluxed at 150 °C for 3 h. Excess hydrazine was distilled off, and the mixture was heated at 210 °C for 4 h. The cooled reaction mixture was neutralized with 5% HCl, and the mixture was extracted with ether. The organic layer was washed with brine and dried ($MgSO_4$). After evaporation of the solvent in vacuo, the crude product was chromatographed on silica gel to give **17b**: 200 mg (35%); mp 110–112 °C (lit.[10b] 116–117 °C); IR (KBr) 2930, 2850, 1460, 1440 cm^{-1}; MS, *m/e* (relative intensity) 150 (M^+, 60), 107 (100), 79 (30); ^{13}C NMR δ 60.44 (s, 2 C), 40.35 (t, 6 C), 24.62 (t, 3 C) [lit.[10b] δ 60.33 (s, 2 C), 40.32 (t, 6 C), 24.57 (t, 3 C)].

Oxidative Degradation of 20a to Spiro[4.6]undecane (25a). To a rapidly stirred solution of 640 mg (3.51 mmol) of **20a** in 60 mL of benzene was added a solution of 1.87 g (4.22 mmol) of lead tetraacetate in 60 mL of benzene. The mixture was stirred for 1 h at room temperature and filtered. The filtrate was dried over K_2CO_3 and concentrated in vacuo followed by column chromatography on silica gel to yield 457 mg of spiro[4.6]undecane-1,8-dione (**24a**): IR 1730, 1695 cm^{-1}.

A solution of the above diketone and a small amount of hydroquinone in 2.1 mL of ethane-1,2-dithiol was added dropwise into 1.5 mL of boron trifluoride etherate cooled in an ice bath. The resulting solution was stirred at room temperature for 69 h. The reaction was quenched by 10% K_2CO_3 solution, and the mixture was extracted with benzene. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo to yield the crude bisethylene thioketal: IR 1450, 1420, 1270, 1200 cm^{-1}.

The thioketal was dissolved in 100 mL of ethanol and refluxed for 4 h with about 15 g of Raney nickel (W-4). The mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo to yield the crude hydrocarbon **25a**. Chromatography on silica gel gave **25a**: 163 mg (22% from **20a**); IR 2920, 2850, 1455 cm^{-1}; MS, *m/e* (relative intensity) 152 (M^+, 32), 96 (73), 95 (83), 82 (100), 67 (88); ^1H NMR δ 1.16–1.80 (m); ^{13}C NMR δ 46.08 (s), 41.33 (t, 2 C), 40.45 (t, 2 C), 29.89 (t, 2 C), 24.53 (t, 2 C), 24.38 (t, 2 C). Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.57; H, 13.14.

Preparation of an Authentic Sample of 25a. Spiro[4.6]-undecan-6-one was prepared by the literature method.[23] The Wolff–Kishner reduction of 3.03 g (18.2 mmol) of the ketone was carried out as described for **17b** to give 1.74 g of the hydrocarbon (63%) which was identical (IR, MS, ^{13}C NMR) with **25a** obtained by the degradation of **20a**.

Oxidative Degradation of 20b to the Keto Ester 27a. To a solution of 675 mg (3.01 mmol) of **20b** in 1.4 mL of pyridine and 5 mL of methylene chloride cooled to 0 °C was added dropwise 0.33 mL (4.52 mmol) of thionyl chloride via a syringe. The resulting solution was stirred at 0 °C for 30 min and then at room temperature for 4 h. The reaction was quenched by ice–water, and the mixture was extracted with methylene chloride. The organic layer was washed with water, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel to give tricyclo[4.3.2.0^{1,5}]undec-4-en-6-yl acetate (**26a**): 513 mg (83%); IR 3060, 1740, 1250 cm^{-1}; MS, *m/e* (relative intensity) 206 (M^+, 28), 146 (76), 136 (100), 135 (91); ^1H NMR δ 1.20–2.12 (m, 13 H, contains s at 1.96), 2.16–2.76 (m, 4 H), 5.04 (t, 1 H); ^{13}C NMR δ 169.97 (s), 154.83 (s), 110.91 (d), 83.69 (s), 55.68 (s), 38.07 (t), 36.06 (t), 35.87 (t, 2 C), 35.48 (t), 33.53 (t), 21.77 (q), 21.25 (t). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.81; H, 9.18.

A solution of 73 mg (0.36 mmol) of **26a** and 103 mg (0.40 mmol) of osmium tetraoxide in 2.4 mL of pyridine was stirred in the dark at room temperature for 44 h. To the resulting brown solution was added a solution of 148 mg (1.44 mmol) of sodium bisulfite in 3.6 mL of water and 1.8 mL of pyridine, and the mixture was stirred for 18 h and extracted with chloroform. The organic layer was washed with 1 N HCl, water, and dried (K_2CO_3). Evaporation of the solvent in vacuo gave the diol: IR 3450, 1735, 1710,[22] 1280, 1080 cm^{-1}.

The crude diol was oxidized by lead tetraacetate as described for the oxidation of **20a** to give the crude keto aldehyde: IR 1760, 1735, 1710, 1240 cm^{-1}.

To the above aldehyde was added a large excess of saturated bromine–water, and the mixture was stirred at room temperature for 30 min. Sodium disulfite solution was added, and the mixture was extracted with ether. The organic layer was washed with brine and dried ($MgSO_4$). Evaporation of the solvent in vacuo gave the

(23) Mousseron, M.; Jacquier, R.; Christol, H. *Bull. Soc. Chim. Fr.* **1957**, 346; *Chem. Abstr.* **1957**, *51*, 13781e.

keto acid which showed carbonyl absorptions at 1760, 1735, and 1710 cm^{-1}.

The crude keto acid was treated with ethereal diazomethane to give the keto ester **27a** (89% from **26a**) which was purified by preparative GLC: IR 1760, 1735, 1720, 1240, 1050 cm^{-1}; MS, *m/e* (relative intensity) 268 (M^+, 17), 208 (38), 170 (53), 125 (51), 43 (100); ^1H NMR δ 0.80–2.56 (m, 17 H, contains s at 2.00), 3.57 (s, 3 H). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.59; H, 7.55.

Oxidative Degradation of 22a to Spiro[5.6]dodecane (25b). The degradation of **22a** to **25b** was carried out as described for **20a**. Lead tetraacetate oxidation of 1.00 g (5.10 mmol) of **22a** gave spiro[5.6]dodecane-1,9-dione (**24b**): 751 mg (76%); IR 1710, 1690, 1125 cm^{-1}. The subsequent thioketal reduction of 326 mg (1.68 mmol) of **24b** afforded the spiro hydrocarbon **25b**: 130 mg (47%); IR 2920, 2850, 1425 cm^{-1}; MS, *m/e* (relative intensity) 166 (M^+, 56), 96 (100), 81 (71), 67 (66); ^{13}C NMR δ 39.72 (t, 2 C), 38.79 (t, 2 C), 35.58 (s), 30.82 (t, 2 C), 26.70 (t), 22.75 (t, 2 C), 22.09 (t, 2 C).

Preparation of an Authentic Sample of 25b. The authentic sample of **25b** was prepared by the literature method.[15] Condensation of 20 g (0.18 mol) of cycloheptanone with 1,5-dibromopentane gave spiro[5.6]dodecan-7-one: 12.5 g (39%); IR 1690 cm^{-1}. The Wolff–Kishner reduction of 5.0 g (27.8 mmol) of the above ketone afforded 1.8 g (39%) of the spiro hydrocarbon which was identical (IR, MS, ^{13}C NMR) with **25b** obtained by the degradation of **22a**.

Oxidative Degradation of 23 to the Keto Ester 27b. The degradation of **23** was carried out in a manner similar to that of **20b**.

Dehydration of 640 mg (3.51 mmol) of **23** with thionyl chloride–pyridine gave tricyclo[5.3.2.$0^{1,6}$]dodec-5-en-7-yl acetate (**26b**): 457 mg (72%); IR 3050, 1740, 1250 cm^{-1}; MS, *m/e* (relative intensity) 220 (M^+, 21), 178 (44), 160 (100, M^+ – AcOH), 136 (68); ^1H NMR δ 1.16–2.12 (m, 17 H, contains s at 1.96), 2.20–2.64 (m, 2 H), 5.60 (t, 1 H); ^{13}C NMR δ 170.71 (s), 148.39 (s), 110.67 (d), 86.30 (s), 40.07 (s), 38.99 (t), 37.04 (t), 35.13 (t, 2 C), 33.27 (t), 24.36 (t), 21.87 (q), 20.40 (t), 20.11 (t). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.18; H, 9.33.

The oxidation of 235 mg (1.07 mmol) of **26b** by osmium tetraoxide gave the diol (IR 3500–3430, 1735, 1710,[22] 1255, 1075 cm^{-1}) which was subjected to lead tetraacetate oxidation to afford the keto aldehyde: IR 1760, 1735, 1720, 1250 cm^{-1}. Treatment of the crude aldehyde with saturated bromine–water gave the keto carboxylic acid (IR 1760, 1735, 1720, 1060 cm^{-1}), and the subsequent esterification with ethereal diazomethane afforded the keto ester **27b**: 172 mg (62% from **26b**); IR 1760, 1735, 1720, 1240 cm^{-1}; MS, *m/e* (relative intensity) 282 (M^+, 7), 184 (43), 55 (30), 43 (100); ^1H NMR δ 1.14–2.60 (m, 19 H, contains s at 2.00), 3.60 (s, 3 H). Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.85; H, 8.13.

Lithium Aluminum Hydride Reduction of 26b to i. A 122-mg sample of **26b** (0.55 mmol) was reduced by lithium aluminum hydride as described above to afford 98 mg of the unsaturated alcohol i (quantitative) which was purified by preparative GLC: IR 3370, 1170, 1140, 1060, 920 cm^{-1}; MS, *m/e* (relative intensity) 178 (M^+, 41), 149 (61), 136 (100), 135 (62); ^1H NMR δ 0.84–2.16 (m, 17 H), 5.32 (t, 1 H). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.47; H, 10.25.

Preparation of Spiro[4.7]dodecane. The Wolff–Kishner reduction of 3.5 g (19.4 mmol) of spiro[4.7]dodecan-6-one[24] afforded spiro[4.7]dodecane: 314 mg (10%); IR 2910, 2860, 1465, 1440 cm^{-1}; MS, *m/e* (relative intensity) 166 (M^+, 17), 95 (64), 82 (100), 67 (94), 41 (66); ^1H NMR δ 1.20–1.80 (m); ^{13}C NMR δ 45.97 (s), 39.39 (t, 2 C), 36.02 (t, 2 C), 28.87 (t, 2 C), 25.14 (t), 24.45 (t, 2 C), 24.00 (t, 2 C). Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.55; H, 13.54.

Registry No. **9**, 5202-23-3; **10**, 42540-17-0; **11**, 38229-67-3; **12**, 38312-61-7; **13**, 88288-17-9; **13** semicarbazone, 88288-19-1; **14**, 42540-18-1; **15**, 88288-18-0; **16**, 88314-90-3; **17a**, 88288-20-4; **17b**, 51027-89-5; **18**, 38312-62-8; **19**, 88288-21-5; **20a**, 88314-91-4; **20b**, 88315-25-7; **22a**, 88314-92-5; **22b**, 88288-23-7; **23**, 88314-93-6; **24a**, 88288-25-9; **24b**, 88288-30-6; **24a** bis(ethylene thioketal), 88288-26-0; **25a**, 184-12-3; **25b**, 181-15-7; **26a**, 81843-01-8; **26a** diol, 88295-42-5; **26a** keto aldehyde, 88288-27-1; **26a** keto acid, 88288-28-2; **26b**, 81843-02-9; **26b** keto aldehyde, 88288-31-7; **27a**, 88288-29-3; **27b**, 88288-32-8; **28**, 88288-24-8; **29**, 88314-94-7; **30**, 88314-95-8; **31**, 88288-22-6; i, 88288-33-9; bicyclo[5.3.0]dec-1-(7)-en-8-one, 769-32-4; *cis-anti-trans*-dimethyl[4.3.2]propellanone, 38343-72-5; *cis*-2-butene, 590-18-1; ethane-1,2-dithiol, 540-63-6; spiro[4.6]undecan-6-one, 73223-32-2; 1,5-dibromopentane, 111-24-0; cycloheptanone, 502-42-1; spiro[5.6]dodecan-7-one, 4728-90-9; spiro[4.7]dodecane, 1197-84-8; spiro[4.7]dodecan-6-one, 3002-04-8.

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Synthesis, Characterization, and Chemistry of Bridgehead-Functionalized Bicyclo[2.2.2]octanes: Reactions at Neopentyl Sites

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This paper reports the synthesis and characterization of a series of 15 new, symmetric, 1,4-disubstituted bicyclo[2.2.2]octyl derivatives. Beyond detailing their syntheses and spectral properties, it describes the scope of synthetic transformations that can be effected at these neopentyl-like centers. The question of a possible direct displacement by hydride at such a site, as per an earlier literature report, is considered, and the limits of this and related substitution reactions are delineated. The scope of reactions at sp^2 centers attached to these positions is also defined.

In the course of a study of micelle-mediated organic reactions, we required a set of substrates that would provide two isolated but equivalent sites for reaction. These two reaction sites had to be separated by a rigid, nonaromatic, spacer group.[2] We have pursued a synthetic program that has led us to the synthesis and characterization of a variety of bridgehead-functionalized bicyclo[2.2.2]-octanes and has allowed us to delineate some of the

(1) NIH Research Career Development Awardee (1983–1988).

(2) The need for spacer rigidity and the preference for a nonaromatic spacer are best understood by reference to our earlier work: Link, C. M.; Jansen, D. K.; Sukenik, C. N. *J. Am. Chem. Soc.* **1980**, *102*, 7798. Sutter, J. K.; Sukenik, C. N. *J. Org. Chem.* **1982**, *47*, 4174.

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