chloride. After 30 min the reaction was quenched with ether (50 mL). Magnesium sulfate (5.0 g) was added to the reaction mixture. Filtration and evaporation of the solvent in vacuo gave 45 mg (90%) of crude keto aldehyde 8 which was homogeneous by TLC analysis [IR (CCl_4) 2700, 1720 cm^{-1}; NMR (CCl_4) δ 9.40 (s, 1 H, CHO), 7.21 (s, 5 H, C_6H_5), 5.80 (s, 2 H, CH = CH), 4.45 (br s, 3 H, C(5) H, CH_2O), 2.63 (m, 2 H, CH_2CO), 2.25 (m, 2 H, C(1) and C(10) protons), 2.03 (s, 3 H, $COCH_3$), 1.18 (s, 3 H, C(5) methyl), 0.91 (d, 3 H, J = 7 Hz, C(10) methyl)].

(1α,3aβ,4β,8aα)-3a,4,5,8a-Tetrahydro-4,8a-dimethyl-1-(phenylmethoxy)-6(1*H*)-azulenone (1). A solution of 44 mg (0.15 mmol) of keto aldehyde 8 in 3.0 mL of 5% potassium hydroxide–methanol solution was stirred at room temperature for 30 min. The reaction was quenched with an aqueous ammonium chloride solution. The product was extracted with ether. The combined ether layers were dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure afforded 40 mg of the intermediate aldol [R_f 0.15 (1:1 ether–hexane)], which was dissolved in 4 mL of benzene containing 1.0 mg of *p*-toluenesulfonic acid. After refluxing for 45 min, the reaction was quenched with powdered sodium bicarbonate, and the solvent was removed in vacuo. The crude hydroazulenone 1 (35 mg) was chromatographed on silica gel. Elution with 1:4 ether–hexane gave 30 mg (72% overall) of pure 1 as a crystalline substance: mp 77–78 °C; IR (CCl_4) 3070, 3025, 2970, 2940, 2900, 2870, 2825, 1670, 1605, 1458, 1385, 1368, 1348, 1305, 1260, 1230, 1215, 1168, 1140, 1085 1055, 1030 cm^{-1}; NMR (250 MHz) (CCl_4) δ 7.28 (br s, 5 H), 6.17 (AB q, 2 H, J = 11.5 Hz, $\Delta\nu_{AB}$ = 185.6 Hz, C(6) and C(7) olefinic protons), 5.77 (s, 2 H, C(2) and C(3), olefinic protons), 4.60 (AB q, 2 H, J = 12.1 Hz, $\Delta\nu_{AB}$ = 33.0 Hz, CH_2O), 4.52 (s, 1 H), 2.97 (dd, 1 H, J = 8.2 and 12.1 Hz), 2.30–2.15 (m, 2 H), 2.01 (heptet, 1 H), 1.16 (s, 3 H), 1.13 (d, 3 H, J = 6.6 Hz); high-resolution mass spectrum, m/e 282.16089 (calcd 282.16198). An analytical sample was prepared by recrystallization from hexanes–ether, mp 79–80 °C.

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.88; H, 7.74.

Acknowledgment. This investigation was supported by a Public Health Service research grant from the National Cancer Institute. We are indebted to George Majetich for numerous discussions and assistance during the course of this investigation.

Registry No. 1, 68241-54-3; 7, 63598-48-1; 8, 73198-39-7; 9, 73198-40-0; 10, 73198-41-1; 10, free acid, 73210-16-9; 11, 73198-42-2; 13 methyl ester, 73198-43-3; 13, 73198-44-4; 14, 73245-79-1; 14, lactol derivative, 73245-80-4; 15, 73198-45-5; 15, aldehyde derivative, 73198-46-6.

Synthesis of Tricyclo[6.2.1.0^{2,6}]undec-2(6)-ene through Acid-Catalyzed Dehydration–Rearrangement of *exo*-Norbornane-2-spiro-1′-cyclopentan-2′-ol

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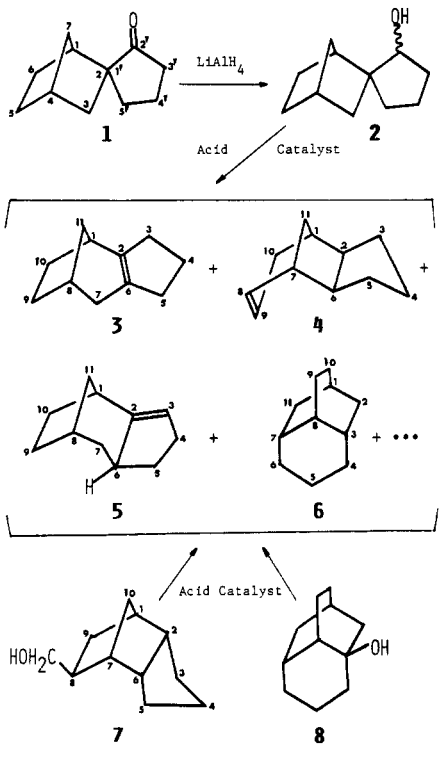
Tricyclo[6.2.1.0^{2,6}]undec-2(6)-ene (3) contains the skeleton of β-patchoulene (1,*exo*-5,11,11-tetramethyl-3),[1] a naturally occurring sesquiterpene. This sesquiterpene is one of the constituents of patchouli oil, an essential oil which is indispensable to the perfume industry because of its characteristic wood-green odor. The structural similarity of 3 to β-patchoulene suggested to us the possibility that some appropriate reactions of 3 would lead to derivatives with desirable fragrance properties. The study[2] of the reactivity of 3 is also of interest[3] from an academic viewpoint, since the compound has a skeleton that has been found only rarely among natural as well as synthetic substances.[3,4]

Scheme I



The tricycloundecene 3 was prepared for the first time by us through phosphoric acid catalyzed dehydration–rearrangement of some tricycloundecanols and tricyclodecylcarbinols.[5] Products of these reactions, however, were distributed among a variety of isomeric tricyclic olefins and alkanes, of which the desired olefin 3 amounted to less than 70%. Herein we report a better synthetic route to the olefin 3 by the dehydration–rearrangement of *exo*-norbornane-2-spiro-1′-cyclopentan-2′-ol (2) (Scheme I). A number of reviews of the dehydration–rearrangement of bicyclic spiro alcohols to internal olefins have been compiled,[6] but no precedent seems to exist for tricyclic spiro alcohols. Formation of 3 from 2 is thus regarded as the first example of a tricyclic analogue of the rearrangement of cyclopentane-1-spiro-1′-cyclopentan-2′-ol to 2,3,4,5,6,7-hexahydroindene.

The starting tricyclic spiro alcohol 2 was prepared by lithium aluminum hydride reduction of the corresponding spiro ketone 1, which was synthesized as described by

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(2) Takaishi, N.; Inamoto, Y.; Aigami, K. *Chem. Lett.* **1979**, 803.

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(5) Takaishi, N.; Inamoto, Y.; Tsuchihashi, K.; Aigami, K.; Fujikura, Y. *J. Org. Chem.* **1976**, *41*, 771.

(6) Dolbier, W. R., Jr. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 3, p 1.

0022-3263/80/1945-2254$01.00/0

Table I. Acid-Catalyzed Dehydration-Rearrangement of the Spiro Alcohol 2 and Related Compounds

run	reaction conditions: reactant[b]	catalyst (g)	solvent (mL)	temp, °C	time, h	product: combined yield, %	constituent, %[a]: 3	4	5	6
1	2	65% H_3PO_4 (40) + p-TS[c] (10)	*n*-octane (40)	130	5	83.3	83.2	2.6	9.8	0.9
2	2	85% H_3PO_4 (8)	*n*-heptane (40)	100	5	77.3	81.3	2.1	10.0	2.9
3	2	I_2 (trace)		150[d]	1	83.1	85.7	1.7	9.8	
4	2	Amberlyst-15 (0.3)	*n*-hexane (3)	70	0.5	88.4	87.8	1.6	9.3	
5	7	85% H_3PO_4 (8)	*n*-heptane (10)	100	20	52.4	57.9	2.8	5.6	10.8
6	7	Amberlyst-15 (1.0)	*n*-hexane (2)	70	27	21.0	33.6	4.8	2.8	38.6
7	8	Amberlyst-15 (1.0)	*n*-hexane (5)	70	0.5	77.1	61.8	1.8	5.2	20.4

[a] Arranged in the order of increasing VPC retention time. Percentages are those of the peak areas. The balance to 100% consisted of several minor products. [b] 1.66 g (10 mmol) was used. [c] p-Toluenesulfonic acid. [d] Under reduced (80 mm) pressure.

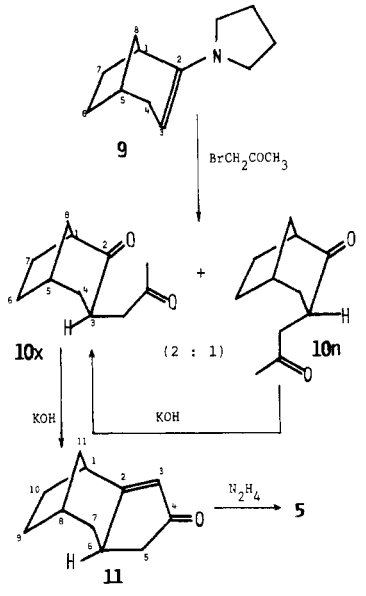
Sauers[7] from cyclopentadiene and a cyclopentanone Mannich base via an in situ elimination and Diels–Alder reaction followed by hydrogenation. The spiro alcohol thus prepared showed a single peak on Golay column VPC, but ^{13}C NMR measurements revealed that it consisted of a ca. 1:1 mixture of two components which are most probably configurational isomers. The mixture per se was used for the isomerization reaction, without determining the configuration of each component.

The spiro alcohol **3** was heated in the presence of an acid catalyst (and a solvent), and the organic layer was separated for analysis on Golay column GC/MS, as in the previous study.[5] Four major products were detected of which three were identified as tricyclo[6.2.1.$0^{2,6}$]undec-2-(6)-ene (**3**), *cis-exo*-6,7-trimethylenebicyclo[3.2.1]oct-2-ene (tricyclo[5.3.1.$0^{2,6}$]undec-8-ene, **4**),[8] and 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **6**).[5,8]

The fourth product was found to be of unknown structure, but its mass spectrum corresponded to a tricycloundecene (M^+ 148). Analysis of its ^1H and ^{13}C NMR spectra indicated the olefinic moiety to be a trisubstituted ethylene. The similarity of the mass spectrum of this unknown compound to that of **3** suggested that the compound possessed a tricyclo[6.2.1.$0^{2,6}$]undecane skeleton. Three tricyclo[6.2.1.$0^{2,6}$]undecenes are consistent with the above spectra: the 2-ene (**5**), the 5-ene, and the 6-ene.[9]

An authentic sample of the 2-ene **5** was synthesized[2] according to the route shown in Scheme II. Alkylation of bicyclo[3.2.1]octan-2-one pyrrolidine enamine (**9**) with α-bromoacetone afforded 3-(2-oxopropyl)bicyclo[3.2.1]octan-2-one (**10**) which comprised a 2:1 mixture of isomers separable on conventional VPC. The mixture was treated with potassium hydroxide, and the minor constituent of **10** completely isomerized to the major one before any cyclization took place. On the basis of the presumably higher stability of the equatorial (exo) isomer **10x** over that of the axial (endo) one **10n**, coupled with the probable[2] preferential reagent attack from the less-hindered exo side in the bicyclooctanone, the exo configuration **10x** was assigned to the major constituent of the alkylation products **10**. The mixture **10** easily cyclized to the tricycloundecenone **11**, Wolff–Kishner reduction of which afforded the target compound **5**. The unknown isomerization product of **2** proved to be identical in all respects with the authentic 2-ene **5**, as determined by VPC and spectrometric (IR, NMR, and mass) analyses.

Scheme II



In the dehydration–rearrangement of the spiro alcohol **2**, a better combined yield of the products (88%) as well as greater selectivity for the olefin **3** (88%) was obtained (Table I) than in any of the same reactions of the tricyclic alcohols studied before.[5] In addition, the most abundant byproduct is **5**, an isomer of **3**, which has a tricyclo[6.2.1.$0^{2,6}$]undecane skeleton. Thus the combined selectivity for the tricyclo[6.2.1.$0^{2,6}$]undecane structure amounted to above 90% in the present isomerization.

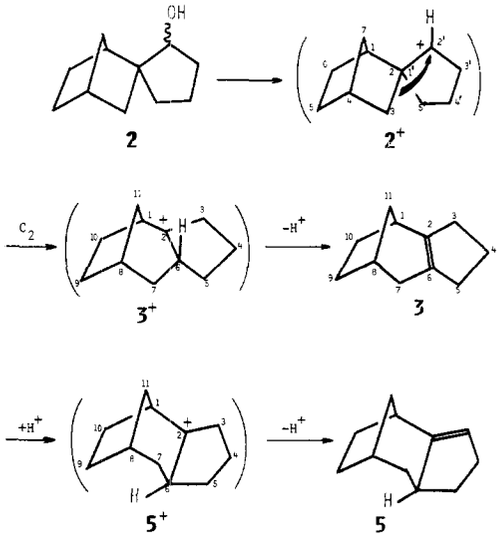
The two tricycloundecenes **3** and **5** appear to be in equilibrium under the present reaction conditions. The ratios of **3** to **5** are ca. 10:1 throughout the experiments listed in Table I, and the same ratios were obtained by prolonged (24 h) treatment of either a pure (97%) sample of **3** or a mixture abundant in **5** (76%) with 85% phosphoric acid at 100 °C.[11]

No appreciable amount of *exo*-norbornane-2-spiro-1′-cyclopent-2′(3′)-ene, the product of simple dehydration

(7) Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850.
(8) Takaishi, N.; Inamoto, Y.; Aigami, K. *J. Org. Chem.* **1975**, *40*, 276.
(9) The 1(10)-, 1(11)-, 7-, 8-, and 8(11)-enes also satisfy the above spectral properties. However, all of these are so-called "anti-Bredt" compounds and most are probably too unstable to be formed under the present reaction conditions.[10]
(10) Fawcett, F. S. *Chem. Rev.* **1950**, *47*, 219. Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464. Keese, R. *Ibid.* **1975**, *14*, 528. Inamoto, Y. *Kagaku (Kyoto)* **1976**, *31*, 326. Fujikura, Y.; Inamoto, Y.; Takishi, N.; Ikeda, H.; Aigami, K. *Chem. Lett.* **1975**, 1203. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2133.

(11) We thank one of the referees for the suggestion to perform these experiments.

Scheme III



without rearrangement, seems to be formed in the present reaction. This is inferred from the fact that the isomerization of **2** gave substantially the same kinds of byproducts as did that of tricyclic alcohols **7** and **8**. The result is in contrast to the reaction of the corresponding bicyclic spiro alcohol cyclopentane-1-spiro-1′-cyclopentan-2-ol in which the simple dehydration product cyclopentane-1-spiro-1′-cyclopent-2-ene was detected, though in a small amount (a few percent).[6]

In the dehydration–rearrangement of the spiro alcohol **2**, the combined yields and ratios of the four major products were dependent upon the kinds and amounts of the catalyst used. Among the catalysts examined, Amberlyst-15, a cation exchange resin, was the most effective, giving the highest combined yield as well as highest selectivity for **3** (Table I, run 4). A cation-exchange resin was successfully utilized for the dehydration–rearrangement of patchouliol to β- and δ-patchoulenes.[3b] In connection with this, the cation-exchange resin caused the same transformation of 3-hydroxy-4-homoisotwistane (**8**),[12] a demethylated analogue of patchouliol. Thus, **8** gave in the presence of Amberlyst-15 the olefins **3** and **5**, the demethylated β- and δ-patchoulenes, respectively (run 7).

A trace of iodine, which converted patchouliol to β-patchoulene,[1a] was also a fairly effective catalyst for the present reaction (run 3). Eighty-five percent phosphoric acid, the catalyst used in the previous study,[5] gave the most inferior result with respect to both combined yield and selectivity (run 2), although addition of some *p*-toluenesulfonic acid to a more dilute (65%) phosphoric acid solution showed a little improvement (run 1). It may be interesting to note that for the dehydration–rearrangement of *exo*-8-(hydroxymethyl)-*endo*-tricyclo[5.2.1.0^{2,6}]decane (**7**),[13] a tricyclodecylcarbinol isomeric to ones studied before,[5] to **3** and **5**, phosphoric acid was yet a better catalyst than was Amberlyst-15 (runs 5 and 6).

Isolation of the internal olefin **3** from the reaction mixture could be done by fractionation on preparative VPC. For example, the product mixture of run 4 when fractionated twice gave **3** with 97% purity in 47% yield, based on **2**.

The higher selectivity for the tricyclo[6.2.1.0^{2,6}]undecane structure in the isomerization of **2** is explained with the inference that the shift of C-3 to the C-2′ cationic center in the cation **2**$^+$ is the only probable process[14] among all the seemingly possible 1,2-alkyl shifts in **2**$^+$ (Scheme III). In total, four 1,2-shifts are conceivable in **2**$^+$: those of C-1, C-3, C-4′, and C-5′. The latter two processes are obviously thermodynamically unfavorable, because they produce cyclobutane-containing structures. The shift of C-1 gives rise to the same skeletal structure as that of **3**$^+$ and, therefore, may appear to explain the experimental result as well. However, this shift is considered less favorable than that of C-3 for the reason that a more strained transition state should be involved which comprises a *parallel* disposition of C-6 and C-7 on the migrating C-1 with respect to the C-2(C-1′)-C-2′ bridge.[15] Thus, the shift of C-3 is the most favorable of all in the cation **2**$^+$.

The shift of C-3 to the C-2′ cationic center should necessarily lead to the *endo*-C-6 configuration in the resulting **3**$^+$. This configuration of **3**$^+$, however, forbids us to formulate the direct formation of **5**, which has the exo configuration of C-6, from **3**$^+$. Therefore, the most reasonable route to **5** seems to consist of reprotonation of the 2(6)-ene **3** from the more congested endo side under product-development control, as in the hydroboration of **3**,[2] to *exo*-C-6-tricyclo[6.2.1.0^{2,6}]undec-2-yl cation **5**$^+$ which has the same *exo*-C-6 configuration as in **5**. This inference is supported by experiments which showed that **3** and **5** interconverted to produce equilibrium mixtures in which **3** and **5** existed in the same 10:1 ratio as in the isomerization of **2**.

The minor products **4** and **6** are formed most plausibly[5,16] by secondary conversions of **3**$^+$ and/or **5**$^+$ via multiple-step skeletal isomerizations. The relatively low selectivities for **3** and **5** in the reactions of **7** and **8** are explained on similar grounds. The substrates **7** and **8** are required to traverse through many reaction steps to reach the skeletal structure **3**, and at each step there exists the possibility that two or more competitive 1,2-alkyl shifts will occur with equal probability to produce a variety of structures.[5,16]

Experimental Section

***exo*-Norbornane-2-spiro-1′-cyclopentan-2′-ol (2).** To a stirred suspension of 1.9 g (50 mmol) of lithium aluminum hydride in 200 mL of dry ether at ambient temperature was added dropwise with efficient stirring a solution of 8.2 g (50 mmol) of *exo*-norbornane-2-spiro-1′-cyclopentan-2′-one (**1**)[7] in 40 mL of ether, and the reaction was heated under reflux with stirring for an additional 2 h. The cooled reaction mixture was diluted successively with 10 mL of ethyl acetate, 10 mL of water, and 6 mL of a 15% sodium hydroxide solution. The precipitates were filtered off, and the filtrate was dried over anhydrous sodium sulfate and concentrated. The residue was fractionally distilled to give 7.4 g (89% yield) of the spiro alcohol **2**: bp 80–82 °C (0.8 mm); n^{20}D 1.5085; IR (neat) 3370, 2940, 2860, 1450, 1290, 1090, 980, 940, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6–1.9 (m, 14 H), 1.9–2.4 (m, 2 H), 2.87 (s, 1 H, OH), 3.4–3.8 (m, 1 H, CHOH); ^{13}C NMR ($CDCl_3$) δ 20.4 (t), 20.6 (t), 25.0 (t), 25.7 (t), 28.9 (t), 29.1 (t), 32.0 (t), 32.7 (t, t), 33.2 (t), 37.3 (d, d), 38.0 (t, t), 40.3 (d, d), 44.0 (t), 44.1 (t), 52.8 (s), 54.6 (s), 79.0 (d, CHOH), 79.4 (d, CHOH).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.8; H, 10.7.

(12) Takaishi, N.; Fujikura, Y.; Inamoto, Y.; Ikeda, H.; Aigami, K.; Ōsawa, E. *J. Chem. Soc., Chem. Commun.* **1975**, 371. Aigami, K.; Inamoto, Y.; Takaishi, N.; Fujikura, Y.; Takatsuki, A.; Tamura, G. *J. Med. Chem.* **1976**, *19*, 536.

(13) Fujikura, Y.; Inamoto, Y.; Takaishi, N.; Ikeda, H. *Synth. Commun.* **1976**, *6*, 199.

(14) Ōsawa, E.; Aigami, K.; Takaishi, N.; Inamoto, Y.; Fujikura, Y.; Majerski, Z.; Schleyer, P. v. R.; Engler, E. M.; Farcasiu, M. *J. Am. Chem. Soc.* **1977**, *99*, 5361.

(15) Fujikura, Y.; Ohsugi, M.; Inamoto, Y.; Takaishi, N.; Aigami, K. *J. Org. Chem.* **1978**, *43*, 2608.

(16) Inamoto, Y.; Aigami, K.; Takaishi, N.; Fujikura, Y.; Tsuchihashi, K.; Ikeda, H. *J. Org. Chem.* **1977**, *42*, 3833, and the preceding papers of the series.

***exo*-6-Tricyclo[6.2.1.0^{2,6}]undec-2-ene (5). (i) Bicyclo[3.2.1]octan-2-one Pyrrolidine Enamine (9).** A mixture comprising 47.0 g (0.38 mol) of bicyclo[3.2.1]octan-2-one,[17] 37.7 g (0.53 mol) of pyrrolidine, and 120 mL of benzene was heated under reflux for 10 h, while the water formed was continuously separated and removed from the reaction mixture. The reaction mixture was concentrated, and the residue was fractionally distilled to give 36.5 g (55% yield) of bicyclo[3.2.1]octan-2-one pyrrolidine enamine (**9**): bp 78–80 °C (0.2 mm); IR (neat) 3050, 2950, 2860, 1390, 1360, 1340, 1290, 1280 cm^{-1}.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.0; H, 10.9; N, 8.1.

(ii) 3-(2-Oxopropyl)bicyclo[3.2.1]octan-2-one (10). To a solution of 34.0 g (0.19 mol) of the enamine **9** in 100 mL of benzene at ambient temperature was added dropwise with stirring a solution of 25.0 g (0.18 mol) of α-bromoacetone in 70 mL of benzene, and the reaction was heated under reflux for 4 h. Water (40 mL) was then added to the reaction, and the resulting mixture was heated under reflux for 2 h. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer and ether extract were washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was fractionally distilled to give 14.5 g (42% yield) of 3-(2-oxopropyl)bicyclo[3.2.1]octan-2-one (**10**): bp 89–91 °C (0.4 mm).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.0; H, 9.2.

Fractionation of the sample on preparative VPC gave the equatorial (exo) isomer **10x** [IR (neat) 2950, 2880, 1720, 1360, 1260, 1190, 1170, 1090, 1050, 1000 cm^{-1}; mass spectrum, m/e (relative intensity) 180 (28, M$^+$), 162 (28), 137 (100), 134 (29), 123 (63), 81 (29), 79 (28), 77 (29), 67 (92)] and the axial (endo) isomer **10n** [IR (neat) 2950, 2880, 1710, 1360, 1320, 1260, 1160, 1120, 1030, 920 cm^{-1}; mass spectrum, m/e (relative intensity) 180 (39, M$^+$), 137 (100), 123 (67), 95 (22), 93 (30), 80 (24), 67 (74)].

(iii) *exo*-6-Tricyclo[6.2.1.0^{2,6}]undec-2-en-4-one (11). A sample (9.5 g, 53 mmol) of the diketone mixture **10** obtained above was mixed with 300 mL of a 20% potassium hydroxide solution and heated under reflux with stirring for 20 h. The reaction mixture was extracted with ether, and the ether solution was concentrated. The residue was purified by elution with ether through an alumina-packed column to give 6.3 g (73%) of *exo*-6-tricyclo[6.2.1.0^{2,6}]undec-2-en-4-one (**11**): IR (neat) 3060, 2950, 1710, 1690, 1280, 1250, 1180, 980, 960, 920, 840, 830, 810 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 23.52 (t), 29.98 (t), 36.06 (d), 38.46 (t), 39.05 (t), 40.02 (t and d), 47.11 (d), 130.14 (d, CH=C), 182.77 (s, CH=C), 208.82 (s, C=O); mass spectrum, m/e (relative intensity) 162 (100, M$^+$), 134 (50), 105 (42), 95 (36), 91 (40), 67 (60), 66 (85).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.6; H, 8.6.

(iv) *exo*-6-Tricyclo[6.2.1.0^{2,6}]undec-2-ene (5). A mixture comprising 3.0 g (18.5 mmol) of the tricycloundecenone **11**, 9.3 g of an 80% hydrazine hydrate solution, 8.3 g of potassium hydroxide, and 100 mL of diethylene glycol was heated under reflux for 3 h and then at 220 °C for 2 h when the water formed and the excess hydrazine were gradually distilled off. The reaction mixture was diluted with water and extracted with *n*-hexane. The hexane extract was washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of the hexane and purification of the residue by preparative VPC gave 1.8 g (66%) of the tricycloundecene **5**: IR (neat) 3050, 1660, 1320, 1290, 1160, 1010, 930, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–3.0 (complex m, 15 H), 5.2–5.4 (br s, 1 H, C=CH); ^{13}C NMR ($CDCl_3$) δ 24.28 (t), 27.45 (t), 29.28 (t), 31.59 (t), 35.61 (t), 36.59 (t), 39.33 (t), 40.49 (d), 51.61 (d), 123.89 (d, C=CH), 143.22 (s, C=CH); mass spectrum m/e (relative intensity) 148 (44, M$^+$), 119 (68), 91 (52), 81 (28), 80 (61), 79 (57), 67 (80), 66 (100).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.2; H, 10.6.

Dehydration–Rearrangement of *exo*-Norbornane-2-spiro-1′-cyclopentan-2′-ol (2) and Related Compounds. The spiro alcohol **2** (or the tricyclodecylcarbinol **7** or 4-homoisotwistan-3-ol, **8**) (1.66 g, 10 mmol) was treated with the catalyst (and the solvent, if any) under the reaction conditions specified in Table I.

When Amberlyst-15 was used as the catalyst (runs 4, 6, and 7), product isolation was conducted by filtration of the resin, which was then washed with the solvent *n*-hexane. The combined filtrate and washings were dried over anhydrous sodium sulfate and concentrated. When phosphoric acid was used as catalyst, separation of the organic layer from the reaction mixture and extraction of the aqueous layer with the same solvent as used in the reaction enabled product isolation (runs 1, 2, and 5). In contrast, products of iodine-catalyzed reactions were distilled from the reaction mixture under diminished pressure as soon as they were formed.

Registry No. **1**, 51269-23-9; **2**, 73210-19-2; **3**, 57496-70-5; **4**, 57526-52-0; **5**, 73245-81-5; **6**, 43000-53-9; **7**, 59728-11-9; **8**, 57234-55-6; **9**, 41455-22-5; **10n**, 73198-85-3; **10x**, 73198-86-4; **11**, 73245-82-6; bicyclo[3.2.1]octan-2-one, 5019-82-9; pyrrolidine, 123-75-1; α-bromoacetone, 598-31-2.

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Improved Procedure for the Oxyamination of Olefins with Trioxo(*tert*-butylimido)osmium(VIII)

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A few years ago, we reported on the vicinal oxyamination of olefins by stoichiometric quantities of *t*-BuNOsO$_3$ (**1**).[2] Although this reaction has been largely supplanted by the osmium-catalyzed vicinal oxyamination reaction,[3] we would like to report some additional observations which serve to improve the original stoichiometric reaction in some cases. In the original reports,[2] it was noted that consistently higher yields of amino alcohol and higher ratios of amino alcohol to diol could be attained with the use of a coordinating solvent such as pyridine. Even so, a number of olefins (e.g., citronellol methyl ether) could not be cleanly converted to amino alcohols by this procedure, and tetrasubstituted olefins (e.g., 2,3-dimethyl-2-butene) yielded only the corresponding diols. We now report that some of these olefins give a much-improved ratio of amino alcohol to diol on reaction of the olefin with **1** in a noncoordinating solvent in the presence of certain tertiary alkyl bridgehead amines.

Although the mechanism of reaction of **1** with olefins is not known, the effect of pyridine on this reaction is almost certainly a result of coordination of pyridine to the metal center at some point along the reaction pathway. However, IR spectroscopy reveals no evidence for complexation of **1** with pyridine.[2b] Griffith and co-workers have noted that a number of tertiary alkyl bridgehead amines, such as quinuclidine (**2**), form adducts with OsO$_4$ which are much more stable than the corresponding pyridine adduct.[4] We now find that reaction of **1** with **2**,

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