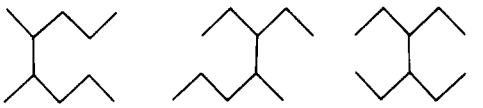
charged in an immersion well reactor (50 mL), flushed with nitrogen gas for 15 min at −10 °C, and then irradiated at room temperature. The light source was a 30-W low-pressure mercury lamp made of Suprasil. Since the alkynes **1–3** are transparent at 254 nm, the effective resonance line of mercury is the radiation at 185 nm. Usually, an alkyne concentration of 0.01 M was employed, since alkynes have extinction coefficients of >1000 L/(mol·cm) at 185 nm,[6] and the light path of our apparatus is 5 mm. In a limited experiment on 1-decyne (**1**), pentane solutions at higher concentrations of 0.02 and 0.04 M were irradiated along with a regular 0.01 M solution under similar conditions. Only negligible differences within the experimental error (±5%) were observed in the product yield between these three runs, suggesting that the incident light at 185 nm was completely absorbed even at 0.01 M concentration.

The quantum yields were determined by cyclooctene actinometer, where the quantum yield for the cis–trans photoisomerization of cyclooctene at 185 nm was taken as 0.33.[15]

Preparative scale photolyses were carried out at a higher concentration (0.05 M) in a large immersion well reactor (200 mL) fitted with a low-pressure mercury lamp and a magnetic stirrer. The irradiation was continued for 8–10 h with periodical analysis on VPC and washing of the lamp surface after every 2 h of irradiation. On removal of pentane from the photolized solution, yellow oil was obtained and was separated by VPC to give pure products.

Identification of Products. The major products, **4**, **6**, **7**, and **8**, except **9**, were identified by direct comparison of IR, ^{1}H and ^{13}C NMR, and mass spectra and the retention time of two or three different VPC columns with the authentic specimens. Compound **5** isolated by VPC had a retention time different from that of decane and showed the following spectra: mass spectrum (70 eV), *m/e* (M^+) 142 ($C_{10}H_{22}$); IR (neat) 2960, 2925, 1460, 1125 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si standard) δ 1.27 (br s, 10 H), 0.93 (br s, 12 H). These spectroscopic features indicate branched decanes with four methyl groups in a molecule. The ^{13}C NMR spectrum in $CDCl_3$ showed ~15 peaks of various intensities in the region of δ 12–48 from Me_4Si. Four intense peaks of them are reasonably attributable to four methyl (δ 15.7) four methylene (δ 22.0, 37.6), and two methine carbons (δ 38.5) of 4,5-dimethyloctane (**5a**), the



5a 5b 5c

dimer of 2-pentyl radical. The other weaker peaks were also attributed to 3-ethyl-4-methylheptane (**5b**) and 3,4-diethylhexane (**5c**) by applying the chemical shift parameters of Lindeman and Adams.[16] The approximate ratio of these isomeric decanes was evaluated from the peak intensities of ^{13}C NMR spectrum as **5a**/**5b**/**5c** = 5:3:1. This suggests the preferencial formation of 2-pentyl radical over 3-pentyl one in accord with the reported results in radical chemistry.[9b]

Product **9** isolated by VPC showed the following spectra: mass spectrum (70 eV), *m/e* (M^+) 122 (C_9H_{14}); IR (neat) 3010 (>C=C—H), 1680 (>C=C<), 1450, 1435, 930, 890, 850, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.3 (br s, 1 H), 0.9–2.2 (m, 13 H). The skeleton of **9** was confirmed by VPC comparison of authentic *cis*-bicyclo[4.3.0]nonane[17] with the hydrogenated product of **9** over 5% Pd on charcoal. Therefore, the product **9** is inferred to be either bicyclo[4.3.0]nona-1-ene or -9-aene. The ^{13}C NMR spectrum of **9** in $CDCl_3$ provided definitive evidence. By comparison with the ^{13}C NMR spectra of 2,3-dimethylcyclohexene and of 1,2-dimethylcyclopentane as model compounds for **9**, each carbon of **9** was assigned as follows: δ 143.5 (C-1), 118.0 (C-2), 42.2 (C-6), 34.7 (C-7), 31.3 (C-5), 30.3 (C-9), 26.4 (C-3), 24.4 (C-8), and 23.8 (C-4).

(15) Although the quantum yield for cis–trans photoisomerization of cyclooctene at 185 nm was reported to be unity [Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* **1978**, *100*, 2589], recently, in a private communication, Srinivasan has corrected the value to be 0.33 and this result will be published soon by Schuchmann, Sonntag, and Srinivasan.

(16) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.

(17) Inoue, Y.; Takamuku, S.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1147.

Tricyclo[5.3.0.0^{1,6}]decan-5-one and Tricyclo[5.4.0.0^{1,6}]undecan-5-one. Synthesis and Selective Transformation to Spiro and Fused Bicyclic Systems

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Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received August 25, 1980*

Abstract: The title compounds (**10** and **11**) were prepared by copper-catalyzed intramolecular cycloaddition of cyclopentenyl (**8**) and cyclohexenyl (**9**) diazo ketones. Reduction of **10** and **11** with lithium in ammonia gave spiro compounds **12** and **14** while exposure to HCl gave chloro ketones **13** and **15**. In contrast, acid-catalyzed methanolysis of **10** and **11** afforded fused bicyclic structures **16** and **17**. Solvolysis of endo and exo alcohols **24–27** in methanol produced cis fused ethers **28** and **29**, which slowly underwent isomerization to the trans structures **30** and **31**. A mechanism involving opening of a cyclopropylcarbinyl cation, either via a bicyclobutonium ion or by a stepwise pathway which entails a subsequent 1,2-alkyl shift, would be consistent with these results.

Cyclic structures which incorporate conjoined rings can be regarded as members of a progression which begins[2] with spiro cyclic systems (connected rings with one shared carbon) and extends through fused (two shared carbons) to bridged frames, incorporating three or more common atoms. Although a large number of methods of broad applicability exist for the construction of fused and bridged ring skeletons, relatively few general strategies are available for the elaboration of spirocyclic structures. Recently, considerable effort has been made to repair this deficiency, and some developments along these lines have been reviewed.[3]

(1) National Institutes of Health Research Career Development Awardee, 1976–1981.

(2) In a formal sense, the family of catenanes (conjoined rings with no shared atoms) would be the first member of this series.

(3) A. P. Krapcho, *Synthesis*, 77 (1978), and references cited.

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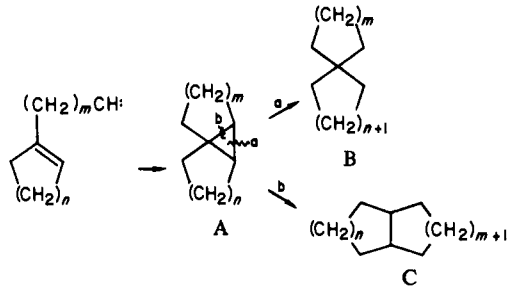
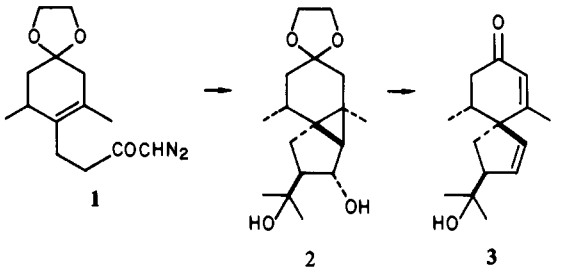
Scheme I



However, there remains a need for methodology which permits synthesis of spiro ring systems in relatively complex molecular environments and which does so in a regio- and stereocontrolled manner. The latter requirement assumes particular significance when it is recognized that many naturally occurring substances that contain a spiro carbon have this atom as an element of chirality.

A general approach to the problem of synthesis of spiro frameworks is illustrated by the concept summarized in Scheme I. This scheme takes advantage of the principle that a tricyclic structure A, generated by the intramolecular addition of a carbenoid to a cyclic olefin, can undergo cleavage of the exterior cyclopropane bond to produce a spiro structure **B** (path a). A particularly elegant application of this idea is found in the synthesis of (±)-epihinesol (**3**) by Deslongchamps,[4] where a tricyclic substance **2**, prepared from diazo ketone **1**, underwent fragmentation to **3** in an acidic medium.

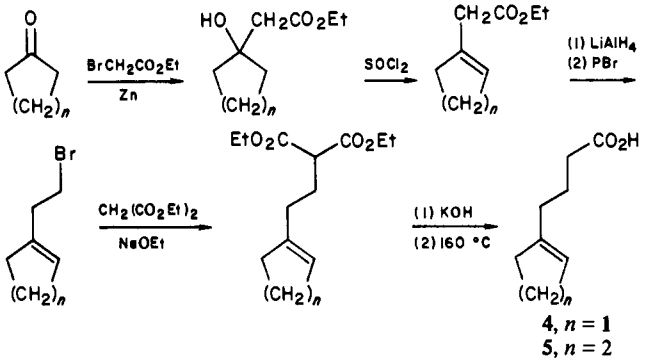


In order to examine this spiroannelation process in a more general context, we undertook the synthesis of two simplified variants of tricyclic structure A. Of particular interest was the possibility of diverting cyclopropane fragmentation toward the alternate mode (Scheme I, path b) which leads to a fused bicyclic skeleton C. In fact, it was hoped that, by appropriate choice of reaction conditions, it might be possible to obtain either spiro or fused structures from a common intermediate. We have found that the transformations in Scheme I can be easily realized and that efficient syntheses of either spiro or fused bicyclic structures can be achieved along these lines.[5]

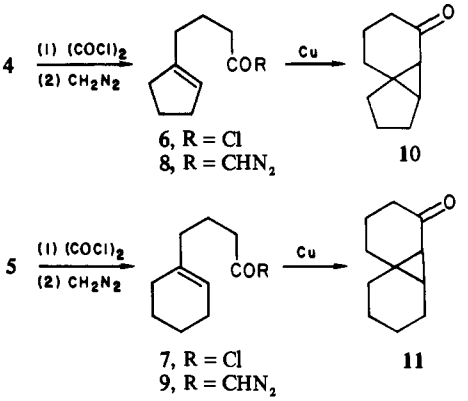
Cyclopentenyl- and cyclohexenylbutyric acids (**4** and **5**) were prepared essentially by the method of Cook and Lawrence (Scheme II).[6] The initial step in this sequence, a Reformatsky reaction of the cyclic ketone with ethyl bromoacetate, was found to be more conveniently effected on a large scale by using the zinc column technique described previously,[7] but otherwise the route shown in Scheme II affords a straightforward means of access to **4** and **5**.

The carboxylic acids **4** and **5** were converted to their respective acyl chlorides **6** and **7** by using oxalyl chloride and thence to the corresponding diazo ketones **8** and **9** with diazomethane. Although the yellow diazo ketones were not fully characterized, their infrared spectra showed the expected strong bands at ca. 2110 and 1640 cm^{-1}, as well as the absence of absorptions due to acyl chloride

Scheme II

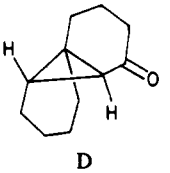


or carboxylic acid functions. Decomposition of these diazo ketones and intramolecular cycloaddition of the resulting carbenoid were found, after considerable experimentation, to be most efficiently accomplished by using a conventional protocol in which **8** or **9**



was treated with finely divided copper bronze powder in hot cyclohexane.[8] This led, after chromatographic purification in each case, to the cyclopropyl ketones **10** and **11**, respectively. The tricyclodecanone **10** was obtained as an oil which showed a carbonyl stretching band at 1685 cm^{-1} in its infrared spectrum, whereas **11** proved to be a crystalline solid (1690 cm^{-1}). Both substances afforded 2,4-dinitrophenylhydrazones which were fully characterized.

Reductive opening of unsymmetrical, conjugated cyclopropyl ketones with lithium in ammonia has been shown by Norin[9] and by Dauben[10] to be a highly specific process in rigid systems. It is found that rupture invariably occurs at the cyclopropane bond which has maximum overlap with the π orbital of the carbonyl group.[11] Conformational analysis of **10** and **11** (see, for example, D) indicates quite clearly that, on this basis, the cyclopropane

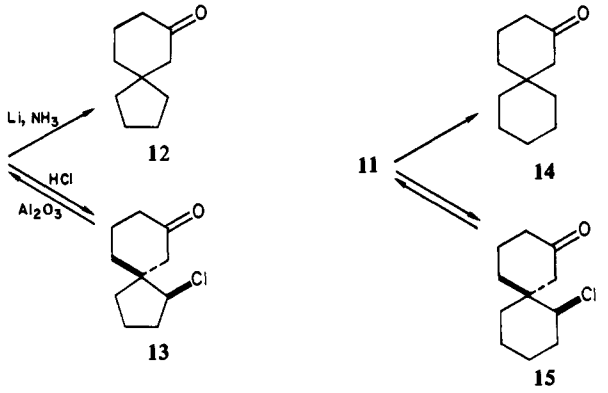


D

linkage favored for scission is the exterior one, (i.e., a in Scheme I). An alternate reduction, involving cleavage of an interior cyclopropane bond (e.g., b in Scheme I), violates the stereoelectronic principle formulated by Norin and Dauben, since this linkage is aligned almost orthogonally to the carbonyl. Thus, reduction of **10** and **11** with with lithium in ammonia containing ether cleanly gave the expected spiro ketones **12** and **14**, respectively. None of the alternate, fused bicyclic ketone could be

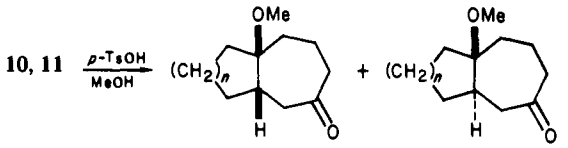
(4) M. Mongrain, J. Lafontaine, A. Belanger, and P. Deslongchamps, *Can. J. Chem.*, **48**, 3273 (1970).
(5) A preliminary account of this work has appeared: J. F. Ruppert and J. D. White, *J. Chem. Soc., Chem. Commun.*, 976 (1976).
(6) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1637 (1935).
(7) J. F. Ruppert and J. D. White, *J. Org. Chem.*, **39**, 269 (1974).
(8) G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961).
(9) T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965).
(10) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).
(11) For an explicit statement of how this orbital overlap should be viewed, see: S. W. Staley in "Selective Organic Transformations", Vol. II, B. S. Thyagarajan, Ed., Wiley Interscience, New York, 1972, p 309.

detected in either case. More surprisingly, however, it was found that the same cleavage mode prevailed when **10** and **11** were

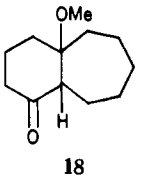


exposed to a two-phase system consisting of ether and concentrated hydrochloric acid. The products, which comprised a single isomer in each case, were established as γ-chloro ketones **13** and **15** on the basis of a one-proton multiplet at ca. δ 3.8 in their NMR spectra, corresponding to a secondary chloride, and a saturated ketone carbonyl absorption at 1715 cm^{-1} in their infrared spectra. Upon chromatography on alumina, **13** and **15** were converted in quantitative yield to the cyclopropyl ketones **10** and **11**, respectively. The facile 1,3-elimination of hydrogen chloride which occurs from **13** and **15** implies the stereochemical relationship of halogen substituent and adjacent spiro carbon shown, since a backside displacement of halide by the ketone enolate is only possible in this orientation. The assigned configuration of chloro ketones **13** and **15** thus requires that opening of the cyclopropane in **10** and **11** occurs with inversion at the carbon to which the halide becomes attached, a result in agreement with observations made by Caine on the opening of tricyclic ketones related to **10** with HBr.[12]

In contrast to the reaction pathway observed with HCl, treatment of **10** and **11** with *p*-toluenesulfonic acid in methanol as solvent was found to yield only fused ring products. Thus, **10** afforded a material which contained a saturated ketone (1712 cm^{-1}) and showed a three-proton singlet at δ 3.3. The absence of other resonances below ca. δ 2.7 established that this was a tertiary methyl ether, which therefore requires that the methoxy substituent be placed at the ring fusion and hence at the carbon which was originally the spiro center. The distinction between **16**, **17** on the one hand and a structure, e.g., **18**, resulting from



16, $n = 1$
17, $n = 2$

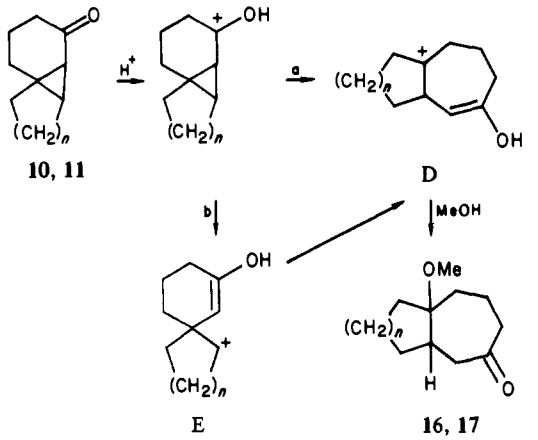


18

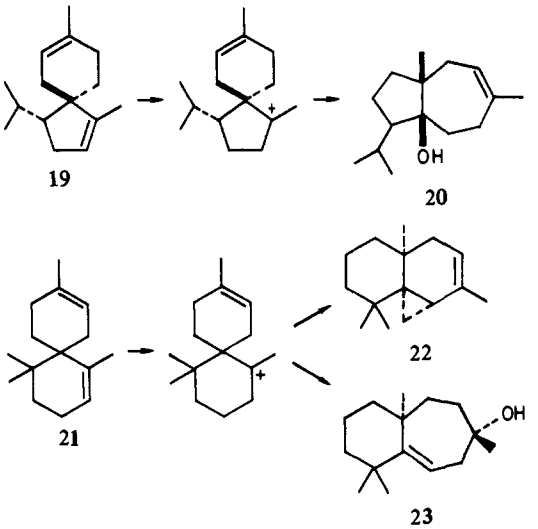
methanolysis of the alternative, internal cyclopropane bond is possible in the case of the undecanone **17**, the NMR spectrum of which displays four protons in two sets (δ 2.30 and 2.69) corresponding to *two* methylene groups α to a ketone. Careful gas chromatographic analysis of **16** and **17** revealed that these consisted in each case of pairs of cis–trans stereoisomers, although the individual isomers could not be separated cleanly.

(12) D. Caine, A. A. Boucugnani, C. Y. Chu, S. L. Graham, and T. L. Smith, *Tetrahedron Lett.*, 2667 (1978).

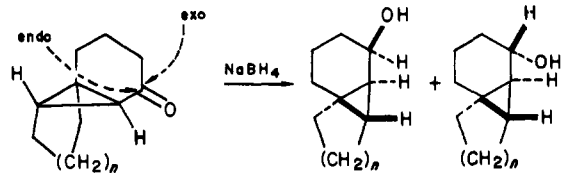
Scheme III



In principle, **16** and **17** are accessible from **10** and **11** by either of two pathways (Scheme III). One of these (path a) could lead from the protonated carbonyl intermediate directly to tertiary carbonium ion D; an alternate route (path b) could invoke cleavage of the exterior cyclopropane bond, as observed previously, to give a secondary carbonium ion E, which could then undergo a Wagner–Meerwein rearrangement to D. A reversible, 1,2-group migration, which interconverts spiro and fused ring systems, has been documented by Zalkow[13] in a correlation of acoradiene (**19**) with carotol (**20**), and by Daeniker[14] and Dauben[15] in a study of the reaction manifold which connects chamigrene (**21**), thujopsene (**22**), and widdrol (**23**).



Unfortunately, stereochemical information which might distinguish between paths a and b in Scheme III was obscured in the methanolysis of **10** and **11** by our inability to identify conclusively stereoisomers in either pair of ketones. In the hope that the derived alcohols might afford more tractable substrates for stereochemical investigation of this rearrangement, **10** and **11** were



10, $n = 1$
11, $n = 2$

24, $n = 2$
25, $n = 3$

26, $n = 2$
27, $n = 3$

(13) L. H. Zalkow, M. G. Clower, M. G. J. Smith, D. Van Derveer, and J. A. Bertrand, *J. Chem. Soc., Chem. Commun.*, 374 (1976); see also L. H. Zalkow and M. G. Clower, *Tetrahedron Lett.*, 75 (1975).
(14) H. U. Daeniker, A. R. Hochstetler, K. Kaiser, and G. C. Kitchens, *J. Org. Chem.*, **37**, 1 (1972).
(15) W. G. Dauben and E. I. Aoyagi, *J. Org. Chem.*, **37**, 251 (1972).

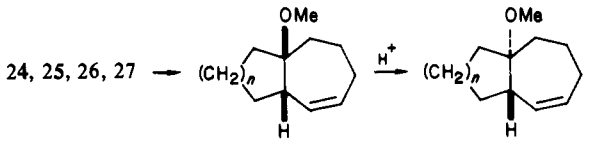
Table I. Acid-Catalyzed Methanolysis of *endo*- and *exo*-Tricyclo[5.4.0.0^{1,6}]undecan-5-ols[a]

alcohol	T, °C	reaction time, h	% conversion	29:30
25	0	0.5	69	9:1
25	20	0.5	75	3:1
25	20	2.0	83	1:1.5
25 + 27 (53:47)	20	0.5	75	3:1

[a] Reactions were carried out at ca 0.01 M in methanol containing one drop of 70% perchloric acid.

each reduced with sodium borohydride in methanol. In both cases, the major alcohol was isolated in pure form by preparative layer chromatography and was assigned endo configuration, **24** and **25**. The minor, exo alcohols, **26** and **27**, could only be obtained as mixtures contaminated with the corresponding endo isomers, but the C*H*OH proton could be clearly distinguished in the NMR spectra of pairs of exo/endo structures. Thus, endo isomers **24** and **25** show this proton at ca. δ 3.9, whereas their exo counterparts, **26** and **27**, exhibit this signal at δ 4.1–4.2, indicating that the endo, pseudoaxial C*H*OH proton experiences the expected deshielding effect due to its orientation with respect to the cyclopropane ring.[16] The stereochemistry observed in the reduction of **10** and **11** is in accord with expectations based on attack by hydride from the less encumbered exo trajectory.

Alcohols **24–27** were found to undergo rapid solvolysis in methanol containing 1 drop of 70% perchloric acid. That the products were again fused structures was apparent from the presence of a tertiary methyl ether at the ring fusion; in addition, the NMR spectra in each instance showed two vinyl protons expected for cycloheptene structures **28–31**. Through a detailed



28, $n = 1$ **30**, $n = 1$
29, $n = 2$ **31**, $n = 2$

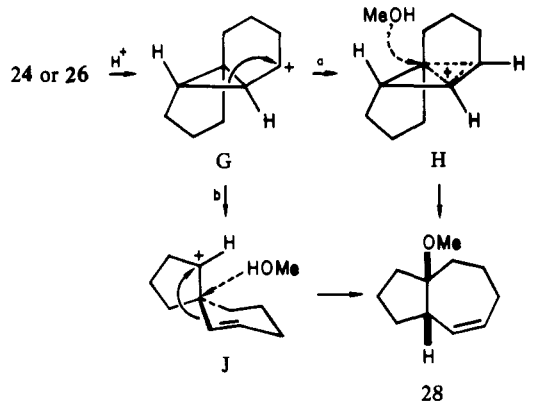
study of this rearrangement it proved possible to assign the ring fusion stereochemistry of the methanolysis products (**28–31**) and to show that the configuration of the hydroxyl group in starting alcohols (**24–27**) exercised no influence on the stereochemical outcome of the reaction. The results are shown in Table I.

It is apparent, first of all, that the rearrangement of carbinols **24–27** at 0 °C is highly stereoselective—a result which would not be anticipated if relatively stable and, perhaps, equilibrating carbonium ions intervened in this process. At 20 °C, however, this stereoselectivity is appreciably diminished; in fact, subjection of the pure stereoisomer formed at 0 °C to methanol containing a trace of acid at 20 °C clearly showed that reaction occurred to give a second bicyclic methyl ether. This stereoisomerization, for the bicycloundecane system **29**, proceeded at a rate only marginally slower at 20 °C than the case for rearrangement of the carbinols **25** and **27** to **29**. For the bicyclodecane **28**, however, isomerization was $<10^{-4}$ times the rate of rearrangement of **24** and **26**. Identical stereochemical results were obtained by starting either with pure endo alcohols **24** and **25** or with mixtures of the endo/exo pairs **24,26** and **25,27**.

The assignment of cis configuration to the methanolysis products **28** and **29** follows from the observation that these products are the result of kinetic control, and that, at least for the bicyclic system containing fused six- and seven-membered rings, equilibration to the more stable trans fusion occurs readily in an acidic medium. The greater reluctance of cis hydroazulene **28** to undergo isomerization to the trans structure **30** apparently reflects an

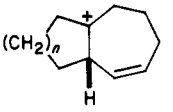
(16) J. Tadanier and W. Cole, *J. Org. Chem.*, **27**, 4610 (1962).

Scheme IV



increased measure of torsional strain for the intermediate cation in this case. Isolation of pure cis and trans isomers, **29** and **31**, by gas chromatography permitted a careful comparison of their NMR spectra, which showed that in **31** the methoxyl protons are shifted downfield by ca. 0.2 ppm relative to the corresponding hydrogens in **29**. Although the effect is small, this downfield shift is consistent with a chair–chair conformation for **31** in which the angular methoxy substituent comes under the deshielding influence of the olefinic linkage.[17] Unfortunately, an insufficient quantity of trans hydroazulene **30** was obtained for accurate comparison of its NMR spectrum with cis isomer **28**. However, it is apparent that in **28** the angular methine proton is shifted downfield by ca. 0.3 ppm as compared with **30**, due to the deshielding effect of the vicinal (cis) methoxy substituent. Not surprisingly, this effect is observed only in **28** (where the five-membered ring enforces eclipsing of substituents at the ring fusion) and is absent in **29**.

The formation of cis ethers **28** and **29** in the methanolysis of **24**, **25**, **26**, and **27** indicates that opening of the cyclopropyl carbinol system takes place with inversion of configuration at the spiro carbon. This would preclude the direct intervention of carbonium ion F in the rearrangement, although this homoallyl



F

cation could be invoked to explain the subsequent isomerization of **28** and **29** to **30** and **31**, respectively.

With the assumption that the first step in the solvolysis of tricyclic alcohols **24–27** is ionization to the cyclopropylcarbinyl cation G, two distinct pathways for the conversion to fused products can be envisaged (Scheme IV). The first (path a) postulates a participatory mechanism involving bicyclobutonium ion H,[18] whereas the second (path b) would proceed in stepwise fashion through initial cleavage of the exterior cyclopropane bond to ion J, which would be followed by a 1,2-alkyl shift and concomitant ring enlargement. Unfortunately, a clear distinction between these two options is not possible with the results at hand. However, it is difficult to see why bicyclobutonium ion H should undergo attack by methanol *exclusively* at the most substituted (spiro) carbon along a trajectory that is seriously obstructed by projecting hydrogens. On the other hand, the stepwise mechanism requires that *only* the vinyl carbon migrate in spiro cation J and that this Wagner–Meerwein rearrangement be accompanied by attack of the nucleophile at the opposite side of the spiro center from which the vinyl carbon has departed. Although precedent exists for both of these processes,[19] a real delineation between paths

(17) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Elmsford, N.Y., 1969, pp 83–88.

(18) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

a and b requires a more thorough characterization of the cationic intermediates involved.

In conclusion, it has been shown that entry to fused and spiro ring frames can be regulated by the selective cleavage under appropriate conditions of interior or exterior cyclopropane bonds in tricyclic ketones **10** and **11** and in their derived alcohols **24–27**. Application of this strategy to syntheses of two spiro sesquiterpenes chamigrene and acorenone B is described in the accompanying paper.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope and are corrected; boiling points are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 137 or 727B infrared spectrophotometer. Ultraviolet (UV) spectra were obtained by using a Cary Model 15 ultraviolet spectrophotometer. Nuclear magnetic resonance (NMR) spectra were determined on a Varian Associates Model EM-360 or HA-100 spectrometer with tetramethylsilane (Me_4Si) as an internal standard. Chemical shifts are reported in δ units. The abbreviations s, d, t, q, m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Mass spectra (MS) and exact mass determinations were obtained by using a CEC-110C spectrometer at an ionizing potential of 70 eV and were provided by Drs. Rottschaefer and Wielesek at the Department of Chemistry, University of Oregon, Eugene, Ore. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. Preparative GLC separations and analysis were carried out by using a Varian-Aerograph Autoprep 700 instrument with (1) a 10 ft × 0.375 in. column of 30% Carbowax 20M on Chromosorb W, or (2) a 5 ft × 0.25 in. column of 20% SE-30 on Chromosorb.

4-Cyclopentenylbutanoyl Chloride (6). A solution of **4** (2.74 g, 17.8 mmol) in 7.5 g (60 mmol) of oxalyl chloride was stirred at room temperature for 0.1 h and then at 40 °C for 0.2 h, during which a colorless gas was evolved. Excess oxalyl chloride was removed in vacuo to give 2.73 g of **6** as a yellow oil: IR (neat film) 2960, 1800, 1445, 1250, 1150, 1022 cm^{-1}. This material was converted to **8** without purification.

4-Cyclohexenylbutanoyl Chloride (7). A solution of **5** (0.50 g, 3.0 mmol) in 1.4 g (11.2 mmol) of oxalyl chloride was stirred at room temperature for 0.1 h and then at 40 °C for 0.2 h, during which a colorless gas was evolved. Excess oxalyl chloride was removed in vacuo to give 0.497 g of crude **7**, as a yellow oil: IR (neat film) 2920, 1800, 1670, 1550, 1223, 1037, 990, 953, 863, 800, 720, 676 cm^{-1}. This material was converted to **9** without purification.

1-Diazo-5-cyclopentenylpentan-2-one (8). A solution of **6** (2.73 g) in 10 mL of hexane was slowly added to an ice-cold, stirred solution of diazomethane, prepared from 10.0 g (56 mmol) of *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide in 110 mL of ether and distilled twice from potassium hydroxide pellets. After 1 h, the solvent was removed in vacuo, and the residue was taken up into ether and filtered. Removal of the solvent gave 2.34 g of **8** as an unstable yellow oil: IR (neat film) 2990, 2110, 1645, 1365, 1150, 1020 cm^{-1}. This material was immediately converted to **10**.

1-Diazo-5-cyclohexenylpentan-2-one (9). A solution of **7** (0.457 g) in 2 mL of hexane was slowly added to an ice-cold, stirred solution of diazomethane prepared from 3.0 g (17 mmol) of *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide in 40 mL of ether and distilled twice from potassium hydroxide pellets. After 1 h, the solvent was removed in vacuo, and the residue was taken up into ether and filtered. Removal of the solvent gave 0.391 g of **9** as an unstable yellow oil: IR (neat film) 2940, 2110, 1640, 1440, 1360, 1138 cm^{-1}. This material was immediately converted to **11**.

Tricyclo[5.3.0.0^{1,6}]decan-5-one (10). A mixture of **8** (2.34 g) and 15.0 g of copper–bronze powder in 900 mL of cyclohexane was heated at 75 °C for 4 h with rapid stirring. A colorless gas was slowly evolved. Filtration, followed by removal of solvent in vacuo and then purification on a column of neutral, Activity II alumina (100 g) gave 0.894 g (33% from **4**) of **10** as a colorless oil: IR (neat film) 2960, 1685, 1320, 1240, 1195, 1080, 1040, 1015, 933, 895, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.8 (m); MS *m/e* 150 (M^+). The 2,4-dinitrophenylhydrazone of **10** was prepared; mp 171–174 °C. Anal. ($C_{16}H_{18}N_4O_4$) C, H, N.

Tricyclo[5.4.0.0^{1,6}]undecan-5-one (11). A mixture of **9** (0.391 g) and 2.0 g of copper–bronze powder in 180 mL of cyclohexane was heated at 65 °C for 0.7 h with rapid stirring. A colorless gas was vigorously evolved after the mixture reached 65 °C. Filtration and solvent removal in vacuo, followed by purification on a column of neutral, Activity II alumina (35 g) gave 0.135 g (38% from **5**) of **11** as colorless prisms: mp 50–51 °C; IR (Nujol mull) 1690, 1443, 1315, 1265, 1247, 1191, 1135, 1038, 947, 914, 883 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15–1.5 (4 H, m), 1.5–2.5 (12 H, m); MS *m/e* 164 (M^+). A sample of **11** gave a 2,4-dinitrophenylhydrazone; mp 173–176 °C. Anal ($C_{17}H_{20}N_4O_4$) C, H, N.

Spiro[5.4]decan-3-one (12). A solution of **10** (146 mg, 0.97 mmol) in 15 mL of distilled ammonia and 2 mL of anhydrous ether was stirred at −40 °C and 27 mg (3.9 mg-atom) of lithium was added in small pieces. After 2.5 h, when the solution had turned blue, 180 mg of ammonium chloride was gradually added, and the cooling bath was removed to allow the ammonia to evaporate. The residue was taken up into 50 mL of ether, washed with aqueous, saturated tartaric acid and with saturated brine, and dried ($MgSO_4$). Filtration and removal of the solvent in vacuo, followed by purification on preparative layer silica gel, gave 77 mg (52%) of **12** as a colorless oil: IR (neat film) 2990, 1712, 1440, 1420, 1304, 1223 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95–2.4 (m); MS *m/e* 152 (M^+). The 2,4-dinitrophenylhydrazone of **12** was prepared; mp 123–132 °C. Anal. ($C_{16}H_{20}N_4O_4$) C, H, N.

Spiro[5.5]undecan-3-one (14). A solution of **11** (152 mg, 0.93 mmol) in 15 mL of distilled ammonia and 2 mL of anhydrous ether was stirred at −40 °C, and 27 mg (3.9 mg-atom) of lithium was added in small pieces. After 2.5 h, when the solution had turned blue, 180 mg of ammonium chloride was gradually added, and the cooling bath was removed to allow the ammonia to evaporate. The residue was taken up into 50 mL of ether, washed with aqueous tartaric acid and with saturated brine, and dried ($MgSO_4$). Filtration and removal of the solvent in vacuo, followed by purification on a column of neutral alumina (Activity II, 25 g), afforded 82 mg (53%) of **14** as a colorless oil: IR (neat film) 2950, 1710, 1443, 1305, 1223, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75–2.1 (16 H, m), 2.1–2.4 (2 H, m); MS *m/e* 166 (M^+). The 2,4-dinitrophenylhydrazone of **14** was prepared; mp 116–141 °C dec. Anal. Calcd for ($C_{17}H_{22}N_4O_4$): H, N, C, 58.95. Found: 58.44.

7-Chlorospiro[5.4]decan-3-one (13). A solution of **10** (248 mg, 1.66 mmol) in 30 mL of ether was stirred at ice temperature and treated dropwise with 5 mL of concentrated hydrochloric acid during 0.1 h. After 41 h, the ether layer was separated, washed with saturated brine and with 5% aqueous sodium bicarbonate, and dried ($MgSO_4$). Filtration and removal of the solvent in vacuo, followed by purification on a column of Activity II silica gel (25 g), gave 221 mg (72%) of **13** as an oil: IR (neat film) 2990, 1710, 1445, 1421, 1307, 1226, 947 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.6 (14 H, m), 3.90 (1 H, t, J = 6 Hz); MS *m/e* 186 (M^+). A 2,4-dinitrophenylhydrazone was prepared; mp 113–116 °C. Anal. ($C_{16}H_{19}ClN_4O_4$) C, H, N, Cl.

Addition of **13** (169 mg, 0.91 mmol) to a column of neutral, Activity II alumina (28 g), followed by elution with ether–hexane over a 7-h period, gave 109 mg (80%) of **10**, by comparison of IR and NMR spectra identical with the product obtained from **8**.

7-Chlorospiro[5.5]undecan-3-one (15). A solution of **11** (289 mg, 1.76 mmol) in 30 mL of ether was stirred at ice temperature and treated dropwise with 5 mL of concentrated hydrochloric acid during 0.1 h. After 0.5 h, the ether layer was separated and washed with saturated brine and with 5% aqueous sodium bicarbonate and dried ($MgSO_4$). Filtration and removal of the solvent in vacuo furnished 339 mg (90%) of **15** as an oil which showed a single spot on silica gel TLC: IR (neat film) 2970, 1715, 1445, 1225, 1138, 931 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.5 (15 H, m), 2.75 (1 H, d, J = 13 Hz), 3.65–3.95 (1 H, m); MS *m/e* 200 (M^+). This substance afforded a 2,4-dinitrophenylhydrazone; mp 113–116 °C. Anal. Calcd for ($C_{17}H_{21}ClN_4O_4$): C, H, Cl, N, 14.46. Found: 14.92.

Addition of **15** (100 mg, 0.5 mmol) to a column of neutral, Activity II alumina (25 g), followed by elution with ether–hexane over a 4-h period gave 74 mg (90%) of crystalline **11**, by comparison of melting point and NMR and IR spectra identical with material prepared from **9**.

***cis*- and *trans*-1-Methoxybicyclo[5.3.0]decan-5-one (16).** A solution of **10** (96 mg, 0.64 mmol) and 60 mg (0.31 mmol) of *p*-toluenesulfonic acid in 10 mL of absolute methanol was maintained at 35 °C for 20 h. After the solvent was removed in vacuo, the residue was taken up into 30 mL of ether, washed with 2 × 25 mL of saturated brine, and dried ($MgSO_4$). Filtration and solvent removal in vacuo, followed by chromatography on a column of neutral Activity II alumina (25 g), gave 78 mg (67%) of **16** as an oil: IR (film) 2990, 1712, 1440, 1308, 1225, 1096 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.6 (15 H, m), 3.30 (3 H, s); MS *m/e* 182 (M^+). Gas chromatography indicated that this product consisted of a major and minor isomer (ca. 4:1), but these could not be separated.

***cis*- and *trans*-1-Methoxybicyclo[5.4.0]undecan-5-one (17).** A solution of **11** (64 mg, 0.39 mmol) and 60 mg (0.31 mmol) of *p*-toluenesulfonic acid in 10 mL of absolute methanol was refluxed for 24 h. After the solvent was removed in vacuo, the residue was taken up in 30 mL of ether, washed with 2 × 25 mL of saturated brine, and dried ($MgSO_4$). Filtration and solvent removal in vacuo, followed by chromatography on a column of Activity II silica gel (20 g), gave 56 mg (73%) of **17** as an

(19) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959), and references cited.

oil: IR (film) 2980, 1710, 1445, 1225, 1185, 1100, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.1 (13 H, m), 2.30 (2 H, t, J = 6 Hz), 2.69 (2 H, d, J = 14 Hz), 3.32 (3 H, s); MS m/e 196 (M^+). Anal. ($C_{12}H_{20}O_2$) C, H. Gas Chromatography indicated that this product consisted of two barely resolvable isomers.

***endo*- and *exo*-Tricyclo[5.3.0.0^{1,6}]decan-5-ol (24 and 26).** A stirred solution of **10** (154 mg, 1.02 mmol) in 20 mL of absolute methanol at ice temperature was treated with 135 mg (3.56 mg-atom) of sodium borohydride for 1.5 h. After the solvent was removed in vacuo, the residue was taken up into ether, washed with aqueous ammonium chloride and with saturated brine, and dried ($MgSO_4$). Filtration and solvent removal in vacuo followed by preparative silica gel TLC gave a fraction containing 33 mg (21%) of a mixture of *endo*-**24** and *exo*-**26** (1:1 by NMR), and another fraction containing 78 mg (50%) of pure **24** which was distilled: bp 60–65 °C (1.0 mm); IR (film) 3400, 2960, 2890, 1440, 1345, 1290, 1150, 1090, 1060, 1045, 1028, 1008, 985, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.65–0.85 (2 H, m), 0.9–2.0 (12 H, m), 2.41 (1 H, br s), 3.72–4.00 (1 H, m); MS m/e 152 (M^+).

***endo*- and *exo*-Tricyclo[5.4.0.0^{1,6}]undecan-5-ol (25 and 27).** A stirred solution of **11** (154 mg, 0.94 mmol) in 20 mL of absolute methanol at ice temperature was treated with 135 mg (3.56 mg-atom) of sodium borohydride for 1.5 h. After solvent removal in vacuo, the residue was taken up into ether, washed with aqueous ammonium chloride and saturated brine, and dried ($MgSO_4$). Filtration and solvent removal in vacuo, followed by preparative silica gel TLC gave a higher R_f fraction containing 66 mg (42%) of a mixture of *endo*-**25** and *exo*-**27** (7:3 by NMR) and a lower R_f fraction containing 62 mg (40%) of pure **25**: IR (film) 3400, 2980, 2900, 1440, 1330, 1280, 1075, 1050, 1012, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.4–0.8 (2 H, m), 0.8–2.1 (15 H, m), 2.3 (1 H, br s), 3.95 (1 H, t, J = 7 Hz); MS m/e 166 (M^+).

***cis*-1-Methoxybicyclo[5.3.0]dec-5-ene (28).** A solution of **24** (77 mg, 0.48 mmol) and 1 drop (22 mg, 0.15 mmol) of 70% perchloric acid in 5 mL of absolute methanol was stirred at ice temperature for 3 h. The solution was neutralized with concentrated, aqueous sodium bicarbonate, diluted with water, and extracted with 2 × 15 mL of ether. The combined extract was dried ($MgSO_4$) and filtered, and the solvent was removed by distillation at atmospheric pressure. Distillation of the residual oil gave 59 mg (75%) of **28**: bp 35–40 °C (0.05 mm); IR (film) 3000, 1450, 1320, 1270, 1200, 1090, 1060, 963 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–2.6 (12 H, m), 2.6–2.9 (1 H, m), 3.20 (3 H, s), 5.3–5.8 (2 H, m); MS m/e 166 (M^+). Anal. ($C_{11}H_{18}O$) C, H.

***cis*- and *trans*-1-Methoxybicyclo[5.4.0]undec-5-ene (29 and 31).** A mixture of **25** and **27** (56 mg, 0.30 mmol, in the ratio of 4:1) and 5 drops (110 mg, 0.8 mmol) of 70% perchloric acid in 5 mL of absolute methanol was stirred at ice temperature for 0.5 h. The solution was neutralized with concentrated aqueous sodium bicarbonate, diluted with water, and extracted with 2 × 15 mL of ether. The combined extract was dried ($MgSO_4$) and filtered, and the solvent was removed by distillation at atmospheric pressure. Vacuum distillation gave 46 mg (73%) of a mixture of **29** and **31** (9:1 by NMR): bp 42–45 °C (0.04 mm). These were separated by preparative gas chromatography to give **29**: IR (film) 2970, 1460, 1355, 1190, 1140, 1095, 943, 910, 870, 793, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–2.2 (14 H, m), 2.47–2.64 (1 H, m), 3.20 (3 H, s), 5.3–5.9 (2 H, m), MS m/e 180 (M^+). Anal. Calcd for ($C_{12}H_{20}O$): H, C, 79.94. Found: 80.45.

Also isolated from the preparative gas chromatogram was **31**: IR (film) 2990, 1450, 1080, 965, 940, 855, 800, 735, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–1.9 (12 H, m), 1.9–2.1 (2 H, m), 2.87–3.04 (1 H, m), 3.34 (3 H, s), 5.4–5.9 (2 H, m); MS m/e 180 (M^+).

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Spiroannelation via Intramolecular Ketocarbenoid Addition. Stereocontrolled Synthesis of (−)-Acorenone B and (±)-α-Chamigrene

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Abstract: The spirobicyclic structures of (±)-α-chamigrene (**7**) and (−)-acorenone B (**6**) were synthesized by means of a copper-catalyzed, intramolecular cycloaddition of diazo ketones **25** and **47**, respectively. The former was prepared from 4-methyl-4-(*p*-methoxyphenyl)pentanoic acid (**8**) and the latter was obtained in optically active form from (*R*)-(+)-limonene (**35**). Reduction of **26** with lithium in ammonia gave **27**, which was transformed to (±)-α-chamigrene (**7**) via olefin **30** and carbinol **32**. The tricyclic ketone **53**, from **47**, was converted via olefin **55** to spiroketone **56**. Introduction of the conjugated olefin afforded (−)-acorenone B (**6**). Alternatively, **53** was reduced with lithium in ammonia to **54** and this, through a parallel sequence, was taken to (−)-4-epiacorenone B (**67**).

In the preceding paper,[2] the synthesis of spiro[4.5]decanone (**3**, n = 2) and spiro[5.5]undecanone (**3**, n = 3) was described, based upon intramolecular addition of the carbenoid derived from **1**, followed by reductive scission of the tricyclic ketone **2** at the perimeter cyclopropane bond (Scheme I). Furthermore, a variation of this plan was shown to be applicable to the preparation of fused ring systems, e.g., **5**, in a stereocontrolled manner via solvolysis of the cyclopropyl carbinol **4**. Thus, related skeletal types can be obtained in discriminative fashion from a common intermediate **2**.[3]

In order to test the feasibility of this approach in functionally more complex systems, we chose to examine routes to (−)-acorenone B (**6**) and (±)-α-chamigrene (**7**), sesquiterpenes of the spiro[4.5]decane and spiro[5.5]undecane class, respectively, along lines exemplified by the sequence **1** → **2** → **3**. In this paper, we present a detailed account of our results, which have led to the

(1) (a) National Institutes of Health Research Career Development Awardee, 1976–1981. (b) Oregon State University. (c) Okayama University.

(2) J. F. Ruppert and J. D. White, *J. Am. Chem. Soc.*, preceding paper in this issue.

(3) For a preliminary account, see J. F. Ruppert and J. D. White, *J. Chem. Soc., Chem. Commun.*, 976 (1976).

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