Intramolecular Cyclopentene Annulation. 2. Synthesis and Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Bicyclo[4.3.0]non-7-en-2-ones

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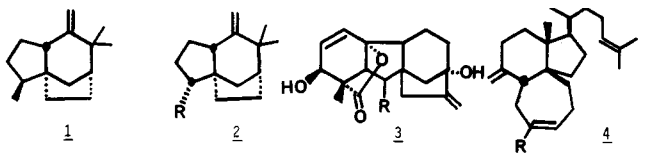
The preparation of several diazonona-6,8-dien-2-ones substituted at positions 1 and 9 is described. Intramolecular cyclopropanation and thermolysis of the resulting vinylcyclopropanes provided functionalized perhydroindanes in useful yields. Detailed ^{13}C NMR analysis of all diastereomers obtained has permitted their unambigous stereochemical assignment. The yields of preparation and the chemical shift data are compared to the results of similar studies in the bicyclo[3.3.0]octane series. The scope and limitation of this internal cyclopentene annulation procedure in the synthesis of hydrindane natural products are indicated.

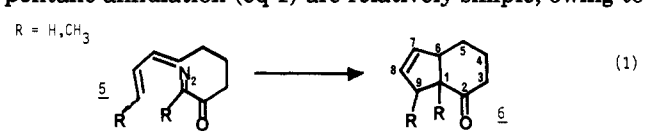
In a previous report[1] we described the synthesis of bicyclo[3.3.0.]octanes via the cyclopropanation–rearrangement sequence of dienic diazo ketones. This study had proved to be a necessary prelude to any synthetic venture into the field of cyclopentanoid terpenes. A commitment had been made to several target molecules, and we were pleased to report the successful construction of the first of these, (±)-hirsutene,[2] by direct application of the above methodology. In an effort to broaden the scope of this new annulation procedure, we contemplated a similar study aimed at bicyclo[4.3.0.]nonanes or perhydroindanes which constitute a structural subunit of several terpenoid classes. Among the synthetically attractive targets we noticed especially the sesquiterpenes of khusane type exemplified by khusane (1) and zizanoic acid (2), diterpenoid gibberellic acid (3), gascardic acid (4), a member of the rare sesterpene class, and various ring-D-oxygenated steroids of the spirostane type.[3,4]



1 2 3 4

R = CO_2H

The common feature bestowed on all of the above compounds during their biogenesis is a 1,2,2,3-tetrasubstituted cyclopentane ring. This observation coupled with the existence of a number of bridged positions around the cyclohexane ring limits severely the use of Diels–Alder strategy as the means of preparation. Although simple perhydroindanes are easily available via the application of an intramolecular Diels–Alder reaction,[5] the peripheral substitution of khusanes, for example, would place heavy demands on the structure of any requisite dienic precursor which could be used to construct this skeleton. On the other hand dienes needed for the intramolecular cyclopentane annulation (eq 1) are relatively simple, owing to

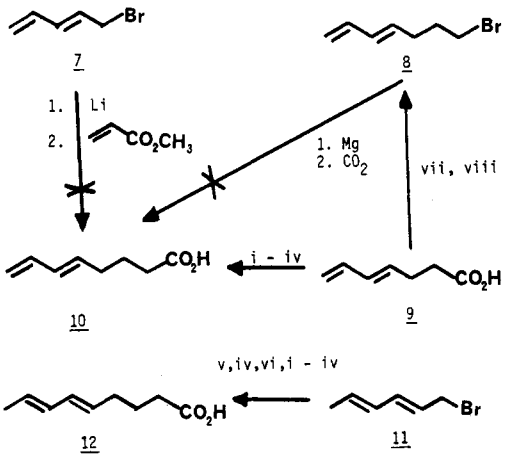


R = H, CH_3 5 6 (1)

the unsubstituted periphery of the cyclopentane ring. Furthermore, the cyclopropanation–rearrangement sequence regiospecifically generates the olefin which may be used to further functionalize compounds of the type 6.

In this report we describe the preparation and ^{13}C NMR spectroscopy of several substituted perhydroindanes

Scheme I[a]



[a] Reagents: (i) $(COCl)_2$/hexane, (ii) CH_2N_2, (iii) $AgO_2CC_6H_5/Et_3N/MeOH$, (iv) KOH/H_2O, (v) $CH_2(CO_2Me)_2$/MeONa, (vi) DMF, 30-min reflux, (viii) $LiAlH_4$, (viii) PBr_3.

possessing the substitution pattern delineated in 6. The differentiability of ^{13}C NMR chemical shifts of C-1 and C-9 substituents in this model study should aid in a facile assignment of diastereomers which will be encountered during the synthesis of perhydroindane natural products.

Results and Discussion

The preparation of the required dienic acids 10 and 12 proved to be more difficult than originally anticipated. All attempts to obtain these acids by "obvious" methods (Scheme I) such as conjugate addition of the dienyl unit derived from the available bromide 7[6] to acrylates[7] or

* Fellow of the Alfred P. Sloan Foundation, 1981–1983.

(1) Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020.
(2) Hudlicky, T.; Kutchan, T. M.; Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6351.
(3) For a structural classification of terpenes, see: Devon, T. K.; Scott, A. I. "Handbook of Naturally Occurring Compounds"; Academic Press: New York, 1972; Vol. II.
(4) For recent synthetic efforts in this area see, for example, the following. Zizaene-type terpenes: Vettel, P. R.; Coates, R. M. *J. Org. Chem.* **1980**, *45*, 5430; Piers, E.; Banville, J. *J. Chem. Soc., Chem. Commun.* **1979**, 1138. Gibberellic acid: Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S.; Keck, G. E.; Gopalan, B.; Larsen, S. D.; Siret, P.; Gras, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 8034. Gascardic acid: Boeckman, R. K., Jr.; Blum, D. M.; Arthur, S. D. *Ibid.* **1979**, *101*, 5060.
(5) See, for example: Roush, W. R.; Gillis, H. R. *J. Org. Chem.* **1980**, *45*, 4283 and references therein.
(6) Mori, K. *Tetrahedron* **1974**, *30*, 3807.
(7) Leyendecker, F.; Jesser, F. *Tetrahedron Lett.* **1980**, 1311. Noyori, R.; et al. *Ibid.* **1980**, 1247.

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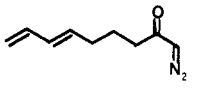
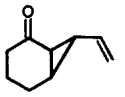
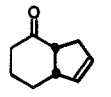
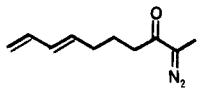
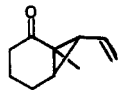
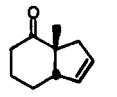
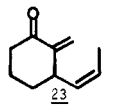
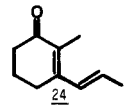
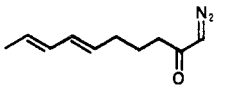
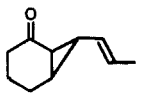
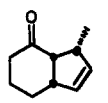
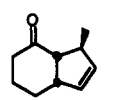
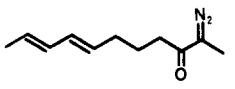
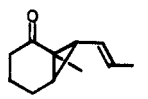
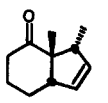
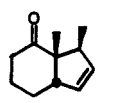
Table I

diazo ketone	vinylcyclopropane, %[a]	bicyclononane, conditions
 13	 17 95%	 21 72% Vycor, 580°C $PbCO_3$
 14	 18 81%	 22 74%, 580°C Vycor;  23 82% Pyrex 400°C;  24
 15	 19 54%	[b]42%  25a; 37%  25b
 16	 20 38%	[b]34%  26a; 26%  26b

[a] Yields represent isolated amounts. [b] Estimated by GC (Carbowax 1500, FID).

Grignard synthesis[8] from heptadienyl bromide 8[9] failed in our hands. Various other methods of diene generation also proved successful or overly costly. These included Pd-catalyzed elimination of allylic acetates,[10] Pd-catalyzed alkylation of vinylic halides,[11] homo-Claisen rearrangement,[12] Wittig reaction,[13] and others.

The one reliable method which could be used in the preparation of linear dienes such as **10** and **12** proved to be the use of Arndt–Eistert reaction.[14] Although this method involves the handling of moderate quantities of diazomethane,[15] it is, with proper precautions,[16] quite safe and completely reproducible. The availability of acid **9**[1] and the high yields of the three-step homologation prompted us to prepare acid **10** in this way (Scheme I).

Similarly, the high degree of reproducibility of the malonate ester synthesis starting from the available sorbyl bromide[6] followed by the Arndt–Eistert homologation furnished us with the substituted acid **12**. It should be noted that syntheses of cyclic dienes or alicyclic dienic acids are *not* plagued by such limited choice of methodologies because of a wider variety of precursory functionalities.[17]

The acids were converted to the diazo ketones **13–16** by using procedures described previously.[1]

Cyclopropanations. The formation of cyclopropanes **17–20** was accomplished regio- and stereospecifically by refluxing dilute solutions of diazo ketones in benzene containing a catalytic amoung of $Cu(acac)_2$. With the exception of the simple vinylcyclopropane **17**, the yields of bicycloheptanes were lower than those observed for the bicyclohexane series.[1] The lower yields were especially noticable with diazoethyl ketones **14** and **16**. A probable solution to this problem lies in the development of a different catalyst for the cyclopropanation of these conformationlly more flexible dienes. We have tried several rhodium-, palladium-, and molybdenum-based systems[18] and obtained slightly higher yields of the vinylcyclopropanes; however, we have not tried to systematically optimize the yields (Table I).

Rearrangements. Pyrolyses of the vinylcyclopropanes were carried out on lead-conditioned Vycor glass between 550 and 600 °C.[1] In the case of methylvinylcyclopropane **18** it proved possible to effect conditions selective for either the retroene reaction, leading to **23**, or the cyclopentene rearrangement, giving the angularly methylated bicyclononane **22**. Paralleling our observations regarding the five-membered-ring analogues,[1,19] the selectivity and the yields of the transformations were acceptable. Enone **24** was identified as a byproduct of the thermolysis at 600 °C.

We have also attempted to effect the cyclopentene rearrangement using $(C_2H_4)_2Rh(acac)$ as previously reported[1] but without much success. The yields of the metal-promoted rearrangements were less than 10%; however, the *stereoselectivity* matched that observed earlier; namely, the isomers **25b** and **26b** (minor products in the pyrolyses) were formed exclusively, albeit in trace amounts.

The bicyclic ketones were found to be extremely volatile. Their recovery from solvents proved difficult even when freeze–drying conditions were employed. Careful chromatography with methylene chloride on silica furnished pure samples of the bicyclononanes **25a,b** and **26a,b** which

(8) Grignard reagents prepared from hexa- and heptadienyl bromides tended to cyclize via an ene reaction.

(9) Available from heptadienoic acid[1] via reduction, mesylation, and displacement with LiBr/acetone in ~65% yield.

(10) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett* **1978**, 2075. Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Ibid.* **1979**, 2301.

(11) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.

(12) Ziegler, F. E.; Nelson, R. V.; Wang, T. *Tetrahedron Lett.* **1980**, 2125.

(13) J. P. Sheth, unpublished observations: several attempts at dienic acid via acid aldehydes and allylic phosponium salts failed.

(14) Bachman, W. E.; Strure, W. S. *Org. React.* **1974**, 38. Hudlicky, T.; Sheth, J. P. *Tetrahedron Lett.* **1979**, 2667.

(15) For the latest procedures on handling large quantities of diazomethane, see: Hudlicky, M. *J. Org. Chem.* **1980**, *45*, 5377.

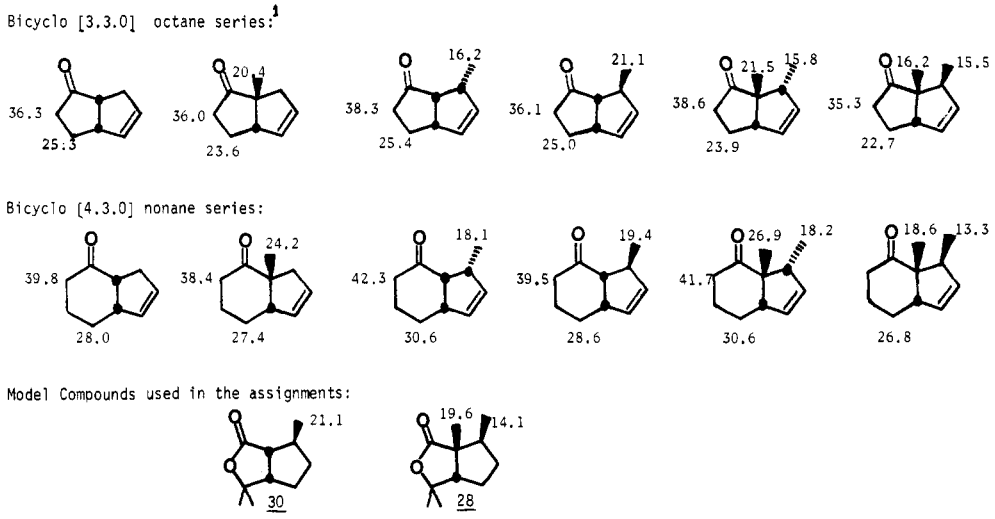
(16) All large-scale work must be done in a well-ventilated hood and behind a safety shield.

(17) Cyclic ketones, alcohols, or epoxides are convenient starting points regarding cyclic dienes.

(18) Doyle, M. P.; Davidson, J. G. *J. Org. Chem.* **1980**, *45*, 1548. Doyle, M. P., private communication.

(19) Hudlicky, T.; Koszyk, F. J. *Tetrahedron Lett.* **1980**, 2487.

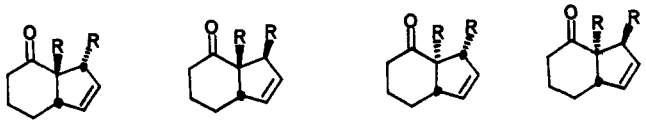
Chart I. Carbon-13 Assignment of Bicyclic Ketones[a]



[a] All chemical shifts reported from Me_4Si (δ 0.0). Only the relevant shifts are indicated; the rest are listed in the Experimental Section.

were required for the stereochemical analysis.

Stereochemical Assignment. The thermolytic rearrangements of the vinylbicyclo[4.1.0.]heptanones could have, in principle, produced all four possible diastereomers of the type **27**. The energetic differences in the cis- vs.

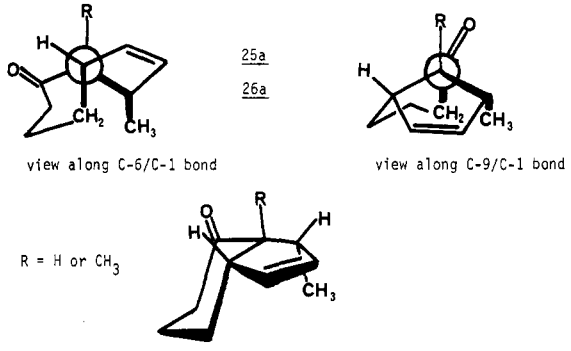


27a **27b** **27c** **27d**

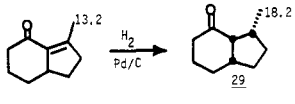
trans-fused perhydroindanes are only subtle for the parent hydrocarbon, with the trans system being marginally more stable.[20] For perhydroind*anones* the cis-fused junction is perferred by ~1 kcal, but for C-6 angularly methylated hyrindanones the trans fusion is again favorable.[21] ^1H NMR spectroscopy could be used to assign stereochemistry of the angularly unsubstituted system provided that the complex pattern of the C-1 hydrogen could be analyzed in terms of the relevant coupling constants. This is not possible at 60 or 100 MHz. In the angularly substituted systems the only stereochemical information derivable from ^1H NMR spectra would be the cisoid vs. transoid coupling constant of H-6 and H-9,[22] but the resolution of these protons is questionable even with the use of a high-field instrument. Clearly, the carbon-13 chemical shifts become the only means of stereoassignment.

The normal shielding arguments can be used to assign relative stereochemistry of the methyl groups at C-1 and C-9.[23] The nearly eclipsed configuration of the two methyls in **26b** (Chart I) results in a drastic mutual polarization of the C–H bonds and an upfield shift of 8.3 ppm for the C-1 methyl and 4.9 ppm for the C-9 substituent. However, one may note that the angular substitution itself has almost no effect on the C-3 and C-5 methylenes in the cyclohexanone portion of the molecules. Likewise, an introduction of a C-9 methyl group on the top face of the molecules as in **25b** or **26b** does not perturb any carbons except that of the angular methyl. The C-3 and C-9 chemical shifts are remarkably constant in the compounds **21**, **22**, **25b**, and **26b**. The introduction of angular methyl in **22** and **26b** rigidifies the system and produces slight shielding between C-5 and C-9 to the extent of ~1 ppm. However, **25a** and **26a** differ drastically in the shifts of these carbons. A study of conformations (Chart II) reveals that a syn-axial 1,3-interaction exists in **25a** or **26a** between the C-3 and C-5 methylenes and the C-9 methyl group.[23] The simple fact that *both* methylenes are affected by this interaction, manifested as a δ *effect* and a *downfield* shift of 3–4 ppm, immediately rules out the trans-fused diastereomers **27c** and **27d**, in which structures these interactions are not possible. Thus the ring-junction stereochemistry is discerned from the existence (or lack) of syn-axial interaction of substituents affecting *both* C-3 *and* C-5 carbons. The relative positions of the C-9 and C-1 groups then follow from the simple shielding interactions of the nearly eclipsed substituents in **26b** as opposed to the more staggered arrangement in **26a**.[24,25]

Chart II



(20) Eliel, E. L.; Allinger, N. L.; Angyal S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1967.
(21) Hamack, M. "Conformation Theory"; Academic Press: New York, 1965.
(22) Ionin, B. I.; Ershow, B. A. "NMR Spectroscopy in Organic Chemistry"; Plenum Press: New York, 1970; p 138. Appel, H. H.; Bond, R. P. M.; Overton, K. H. *Tetrahedron* **1963**, *19*, 635.
(23) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1978.
(24) The methylated pulegonic acid lactone **28** was used as a model with regard to the relative stereochemistry of the two methyls.
(25) We have prepared ketone **29** by a procedure adopted from Abbott and Spencer (*J. Org. Chem.* **1980**, *45*, 5398); the hydrogenation product of **25a** and **29** proved to be identical.



The ^{13}C NMR chemical shift data for the compounds in Chart I will be of tremendous use in rapid assignment of diasteromeric intermediates encountered during the actual syntheses of natural products.

Conclusion

Having now completed the two major model studies concerning the internal cyclopentene annulation methodology (closures of five- and six-membered rings), we can turn our attention to the applications. This method provides a useful complement to the Diels–Alder reaction, as almost any dienic precursor can be altered at one terminus into either a *dienophile* or a *carbenoid*, thus extending the intramolcular annulation methodologies to closures of five-membered rings. The ultimate problem which must be answered in the long run is the *condition* of the cyclopentene rearrangement. We are presently investigating the possibilities of "direct" 1,4-additions via either metallocarbene complexes or acid catalysis, as well as attempting to perfect the metal-promoted rearrangement. We also hope to report soon on the total synthesis of khusanes via this methodology.

Experimental Section

Boiling points are uncorrected. ^1H NMR spectra were determined at 60 MHz on a Varian T-60 spectrometer or at 80 MHz on a Varian CFT-20 spectrometer. ^{13}C NMR spectra were determined at 100 MHz on a Varian CFT-20 spectrometer. Chemical shifts are reported in parts per million relative to internal tetramethylsilane. Infrared spectra were recorded on a Pye-Unicam 3-300 infrared spectrophotometer. Mass spectra were obtained on a Du Pont 20-491 instrument (low resolution) or on a double-focusing (high-resolution instrument) Du Pont 21-110C.

Anhydrous ether was Mallinckrodt reagent grade and was used without further purification. Benzene was Fisher reagent grade and was used without further purification. Column chromatography was performed by using Macherey Nagle and Co. silica gel 60 (70–270 mesh). All nonhydrolytic reactions were performed under nitrogen atmosphere.

5,7-Octadienoic Acid (10). A solution of 10.27 g (68.5 mol) of 1-diazo-5,7-octadien-2-one[1] in 103 mL of absolute methanol was treated at room temperature over 15 min with a slurry of 1.37 g (6.0 mol) of silver benzoate in 14 mL (0.19 mol) of triethylamine. After the mixture was stirred further for 1 h, the solvent was removed, the residue was taken up in ether, and the ethereal solution was washed successively with dilute hydrochloric acid, saturated sodium bicarbonate, and brine. Drying over sodium sulfate followed by solvent removal afforted methyl 5,7-octadienoate as an oil [8.82 g (84%); IR (neat) 1733 cm^{-1}], suitable for hydrolysis. A mixture of 8.82 g (57.3 mol) of crude ester, 11.0 g (0.19 mol) of potassium hydroxide, 49 mL of methanol, and 49 mL of water was refluxed for 2 h. After the mixture was diluted with water and extracted with ether, the aqueous phase was acidified with hydrochloric acid and extracted with methylene chloride. Drying the extracts over sodium sulfate followed by solvent removal and distillation gave 6.41 g (80%, 67% from diazo ketone) of **10** as an oil: bp 80 °C (0.5 mm); IR (neat) 3084, 1707, 1649, 1604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53–2.56 (m, 6 H), 4.80–6.65 (m, 5 H), 11.91 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.1 (t), 31.7 (t), 33.3 (t), 115.2 (t), 132.1 (d), 133.4 (d), 137.0 (d), 179.6 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 140 (30, M^+), 122 (25), 111 (26), 85 (70), 80 (75), 67 (70), 55 (60), calcd for $C_8H_{12}O_2$ 140.0837, found 140.0839.

5,7-Nonadienoic Acid (12). Methyl 5,7-nonadienoate was obtained as above from 15.0 g (91.5 mol) of 1-diazo-5,7-nonadien-2-one,[1] 1.84 g (8.0 mmol) of silver benzoate, and 18.8 mL (0.25 mol) of triethylamine in 138 mL of absolute methanol as an oil [12.6 g (82%); IR (neat) 1734 cm^{-1}] which was hydrolyzed as described above in a solution of 14.7 g (0.25 mol) of potassium hydroxide in 67 mL of methanol and 67 mL of water to give, after distillation, 10.1 g (88%, 72% from diazo ketone) of **12** as an oil: bp 85 °C [bath temperature (0.2 mm)]; IR (film) 3028, 1704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.56 (m, 6 H), 4.80–6.65 (m, 5 H), 11.91 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.0 (q), 24.3 (t), 31.8 (t), 32.1 (t), 33.4 (t), 127.4 (d), 130.1 (d) 131.5 (d), 180.4 (s); mass spectrum (80 eV), *m/e* (percent of base peak) 154 (22, M^+), 94 (50), 80 (40), 79 (base peak), 53 (25), calcd for $CgH_{14}O_2$ 154.0994, found 154.0990.

Preparation of Acid Chlorides. A 0.23 M solution of the acid in hexane was refluxed with a threefold excess of oxalyl chloride for 1 h. Hexane and oxalyl chloride were removed by distillation at atmospheric pressure, and the acid chloride was distilled under vacuum. The following acid chlorides were prepared according to the general procedure described above.

5,7-Octadienoyl chloride: 80%; bp 36–39 °C (0.15 mm); IR (neat) 1798 cm^{-1}.

5,7-Nonadienoyl chloride: 86%; bp 45 °C [bath temperature (0.2 mm)]; IR (neat) 1799 cm^{-1}.

Preparation of Diazo Ketones.[1] The appropriate acid chloride was added dropwise to an ethereal solution of diazomethane or diazoethane at 0 °C.[1] The solution was permitted to stand for 0.5 h, boiled briefly to expell excess diazoalkane, and evaporated to give pure diazo ketones as pale yellow oils. If the corresponding esters were the contaminants, analytically pure diazo ketones were obtained from a rapidly performed chromatography on silica gel (methylene chloride).

1-Diazo-6,8-nonadien-2-one (13): 94%; IR (neat) 2092, 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48–2.5 (m, 6 H), 5.33 (s, 1 H), 4.77–6.63 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.5 (t), 31.9 (t), 39.9 (t), 54.3 (d), 115.1 (t), 132.0 (d), 133.9 (d), 137.1 (d), 194.6 (s); mass spectrum, calcd for $C_9H_{12}N_2O$ *m/e* 164.0950, found *m/e* 164.0945.

2-Diazo-7,9-decadien-3-one (14): 95%; IR (neat) 2065, 1637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–2.63 (m, 6 H), 1.97 (s, 3 H), 4.83–6.65 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 8.2 (q), 24.1 (t), 31.9 (t), 36.8 (t), 62.0 (s), 115.2 (t), 131.9 (d), 133.8 (d), 137.1 (d), 194.2 (s).

1-Diazo-6,8-decadien-2-one (15): 97%; IR (neat) 2097, 1639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48–2.52 (m, 6 H), 1.70 (d, 3 H), 5.15 (s, 3 H), 5.08–6.17 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.0 (q), 24.7 (t), 31.9 (t), 39.9 (t), 54.4 (d), 127.4 (d), 130.4 (d), 131.4 (d), 131.5 (d), 194.9 (s); mass spectrum, calcd for $C_{10}H_{14}N_2O$ *m/e* 178.1106, found *m/e* 178.1110.

2-Diazo-7,9-undecadien-3-one (16): 98%;, IR (neat) 2064, 1639, 1629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52–2.58 (m, 6 H), 1.70 (d, 3 H), 1.78 (s, 3 H), 5.13–6.17 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 8.3 (q), 18.1 (q), 24.5 (t), 32.1 (t), 37.1 (t), 61.4 (s), 130.4 (d), 130.6 (d), 131.5 (d), 131.6 (d), 194.5 (s).

Preparation of Vinylcyclopropanes. A 0.05 M solution of the diazo ketone in benzene was refluxed with 10 wt % of copper(II) acetoacetonate for 1 h. After removal of solvent, the residue was chromatographed on silica gel, eluting with methylene chloride. Removal of solvent afforded the vinylcyclopropanes as colorless oils.

7β-Ethenyl-(1,6β)-bicyclo[4.1.0]heptan-2-one (17): 95%; IR (neat) 1685, 1639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47–2.53 (m, 9 H), 4.83–5.80 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 18.7 (t), 21.0 (t), 25.1 (d), 27.5 (d), 34.4 (d), 36.9 (t), 114.5 (t), 137.9 (d), 206.5 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 136 (25, M^+), 121 (10), 108 (10), 93 (20), 81 (85) 80 (base peak), 67 (15), 53 (10), calcd for $C_9H_{12}O$ 136.0888, found 163.0889.

1β-Methyl-7β-ethenylbicyclo[4.1.0]heptan-2-one (18): 81%; IR (neat) 1681, 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 15.1 (q), 1.18 (s, 3 H), 1.5–2.6 (m, 8 H), 4.8–6.4 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 15.1 (q), 20.4 (t), 21.9 (t), 31.7 (d), 32.4 (d), 36.1 (s), 36.8 (t), 117.5 (t), 135.2 (d), 209.3 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 150 (20, M^+), 134 (22), 122 (15), 107 (18), 93 (35), 80 (40), 79 (base peak), calcd for $C_{10}H_{14}O$ 150.1045, found 150.1049.

7β-(Prop-1-en-1-yl)-(1β,6β)-bicyclo[4.1.0]heptan-2-one (19): 54%; IR (neat) 1686, 1639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45–2.38 (m, 12 H), 4.77–5.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.3 (q), 18.3 (t), 20.7 (t), 24.6 (d), 34.0 (d), 36.4 (t), 125.3 (d),130.1 (d), 206.4 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 150 (75, M^+), 121 (55), 107 (50), 94 (72), 79 (base peak), calcd for $C_{10}H_{14}O$ 150.1045, found 150.1047.

1β-Methyl-7β-(prop-1-en-1-yl)bicyclo[4.1.0]heptan-2-one (20): 38%; IR (neat) 1679, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.28–2.50 (m, 8 H), 1.68 (d, 3 H), 4.27–4.87 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.4 (q), 17.6 (q), 19.9 (t), 21.4 (t), 30.3 (d), 31.7 (d), 35.2 (s), 36.1 (t), 127.0 (d), 128.0 (d), 208.0 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 164 (base peak, M^+), 156 (60),

142 (90), 141 (85), 135 (85), 105 (70), 93 (40), 79 (60), calcd for $C_{11}H_{16}$ 164.1201, found 164.1196.

Thermolysis of Vinylcyclopropanes. The appropriate vinylcyclopropanes were evaporated through a horizontally situated hot tube (Vycor or Pyrex) at a specified temperature. The glass had been conditioned prior to use with a slurry of lead carbonate in water. The actual distillation of material through the columns took 2–10 min. The eluents were condensed under vacuum (0.05–0.010 mm) in a liquid nitrogen cooled trap. Crude mixtures were then purified by column chromatography on silica gel (methylene chloride). In this manner there were thus obtained the following.

***cis*-Bicyclo[4.3.0]non-7-en-2-one (21)**: at 580 °C; 72%; IR (neat) 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38–2.80 (m, 10 H), 5.18–5.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.0 (t), 28.0 (t), 34.7 (t), 39.8 (t), 46.8 (d), 50.1 (d), 130.4 (d), 134.5 (d); mass spectrum (70 eV), *m/e* (percent of base peak) 136 (20, M^+), 108 (30), 92 (25), 81 (base peak), 80 (95), 66 (20), calcd for $C_9H_{12}O$ 136.0888, found 136.0890.

1-Methyl-*cis*-bicyclo[4.3.0]non-7-en-2-one (22): at 580 °C; 74% IR (neat) 1700, 1623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3 H), 1.48–3.08 (m, 9 H), 5.47–5.77 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.3 (t), 24.2 (q), 27.4 (t), 38.4 (t), 43.5 (t), 54.1 (d), 54.5 (s), 129.6 (d), 134.4 (d), 216.5 (s); mass spectrum (70 eV) , *m/e* (percent of base peak), 150 (80, M^+), 135 (70), 121 (70), 107 (45), 93 (25), 79 (80), 41 (base peak), calcd for $C_{10}H_{14}O$ 150.1045, found 150.1049.

2-Methylene-3-(*cis*-prop-1-en-1-yl)cyclohexanone (23): at 400 °C; 82%; IR (neat) 1685, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (br s, 2 H), 1.75 (dd, J = 7, 1 Hz, 3 H), 1.80–2.40 (m, 4 H), 3.60 (br m, 1 H), 5.20 (m, 1 H), 5.80–6.20 (m, 2 H), 6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.1 (q), 27.6 (t), 27.7 (t), 37.6 (t), 39.9 (d), 117.4 (t), 126.2 (d), 131.5 (d), 147.9 (s), 206.4 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 300, (dimer, base peak), 150 (52, M^+), 135 (55), 121 (30), 108 (30), 93 (55), 79 (50), calcd for $C_{10}H_{14}O$ 150.1045, found 150.1044, calcd for $C_{20}H_{28}O_2$ (dimer) 300.2089, found 300.2097.

9β-Methylbicyclo[4.3.0]non-7-en-2-one (25a) and Its 9α Epimer 25b. Pyrolysis of cyclopropane **19** gave, at 580 °C, 42% **25a** and 37% **25b** with ~20% of enone by products.

25a: IR (neat) 1700, 1632, 1612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (d, 3 H), 0.71–3.13 (m, 9 H), 5.67–5.77 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.1 (q), 22.8 (t), 30.6 (t), 42.3 (t), 42.7 (q), 46.0 (d), 52.4 (d), 132.9 (d), 134.8 (d), 215.2 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 150 (70, M^+), 135 (35), 121 (40), 94 (50), 79 (base peak), calcd for $C_{10}H_{14}O$ 150.1045, found 150.1047.

25b: IR (neat) 1701, 1609 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (d, 3 H), 0.70–5.03 (m, 9 H), 5.48–5.87 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.4 (q), 22.1 (t), 28.6 (t), 39.5 (t), 43.0 (d), 46.7 (d), 58.8 (d), 133.5 (d), 135.6 (d), 213.9 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 150 (65, M^+), 135 (15), 121 (90), 107 (40), 94 (50), 79 (base peak), calcd for $C_{10}H_{14}O$ 150.1045, found 150.1043.

1α,9β-Dimethyl-*cis*-bicyclo[4.3.0]non-7-en-2-one (26a) and Its 9α Epimer 26b. Pyrolysis of cyclopropane **20** at 580 °C gave 34% **26a** and 26% **26b** in addition to ~25% of enone byproducts.

26a: IR (neat) 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (d, 3 H), 1.22 (s, 3 H), 1.38–2.93 (m, 8 H), 5.42–5.73 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.2 (q), 22.1 (t), 26.9 (q), 30.6 (t), 41.7 (t), 51.9 (d), 54.2 (d), 54.8 (s), 132.2 (d), 133.9 (d), 216.1 (s); mass spectrum (70 eV), *m/e* (percent of base peak) 164 (base peak, M^+), 135 (80), 121 (70), 107 (65), 93 (95), 79 (60), calcd for $C_{11}H_{16}O$ 164.1201, found 164.1198.

26b: IR (neat) 1702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (d, 3 H), 1.00 (s, 3 H), 1.40–3.00 (m, 8 H), 5.40–5.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.3 (q), 18.6 (q), 21.6 (t), 26.6 (t), 38.5 (t), 44.1 (d), 52.7 (d), 56.2 (s), 132.9 (d), 136.2 (d); mass spectrum (70 eV), *m/e* (percent of base peak) 164 (base peak, M^+), 149 (75), 135 (80), 121 (55), 107 (60), 93 (65), 79 (40), calcd for $C_{11}H_{16}O$ 164.1201, found 164.1204.

2aα,3α,6,6-Tetramethyl-(5aα)-cyclopentano[2,3-*c*]-2-oxotetrahydrofuran (28). Pulegonic acid lactone[26] (1.5 g, 0.0089 mol) in 1 mL of dry tetrahydrofuran was added at −78 °C to a solution of 1.1 equiv of lithium diisopropylamide [from 0.992 g (0.0098 mol) of diisopropylamine, and 6.55 mL of a 1.5 M solution (0.0098 mol) of hexamethylphosphoramide as a complexing agent]. The yellow-orange solution was permitted to stir at −78 °C for 10 min and then allowed to warm up to −40 °C during an additional 10 min. Methyl iodide (6 g, 0.044 mol, 4.5-fold excess) was added, and the reaction mixture was warmed to room temperature (20 min) and stirred for additional 1.5 h. Quenching with 0.1 N HCl, extraction with three portions of ethyl ether, washing of the ether layer with six 5-mL portions of H_2O, drying, and evaporation yielded 1.48 g (92%) of almost pure methylated product (**28**): IR (neat) cm^{-1} 1748; ^1H NMR ($CDCl_3$) δ 1.0 (d, 3 H, J = 7 Hz), 1.22 (s, 3 H), 1.36 (s, 3 H), 1.42 (s, 3 H), 1.7 (m, 2 H), 2.2 (m, 2 H), 2.6 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 19.6 (q), 24.5 (q), 26.5 (t), 31.1 (q), 33.8 (t), 42.2 (d), 54.5 (s), 55.7 (s), 55.7 (d), 82.9 (s), 181.8 (s).

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