(s, 3), 2.73 (d, 2, J = 2 Hz), 2.45 (d, 2, J = 2 Hz), 1.51 (q, 4, J = 7 Hz), 0.82 (t, 6, J = 7.1 Hz); IR (neat) 2960, 2880, 2860, 1730, 1680, 1460, 1340, 1270, 1200, 1180, 1130, 1080, 1020, 910, 865, 800 cm^{-1}; GC t_R 13.2 min. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.26; H, 9.74.

The spectral data for methyl 5-ethyl-3-methylene-5-heptenoate (**12**, E + Z isomers) are as follows: NMR (CCl_4) δ 5.32 and 5.18 (2 q, 1, J = 6.5 Hz), 4.87 (br s, 2), 3.62 (s, 3), 2.90, 2.81, and 2.76 (3 br s, 4), 1.95 (m, 2), 1.59 and 1.56 (2 d, 3, J = 6.5 Hz), 0.91 and 0.93 (2 t, 3, J = 7 Hz); IR (CCl_4) 2960, 2880, 1740, 1460, 1430, 1330, 1230, 1210, 1150, 1000, 970, 900 cm^{-1}; GC t_R 7.5 min; mol wt calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1304.

Reaction of Methylenecyclohexane with Propadienyl Phenyl Sulfone (13).[12] $EtAlCl_2$ (1.0 mL, 1.57 mmol, 0.9 equiv) was added to a solution of **13** (0.319 g, 1.77 mmol) in 10 mL of CH_2Cl_2 at 0 °C under N_2. Methylenecyclohexane (0.162 g, 2.0 mmol) was added. The solution was allowed to warm to 25 °C and was stirred for 14 days. Normal workup gave 0.414 g of crude product. Chromatography of 0.217 g on 10 g of silica gel with 1:2 hexane–ethyl acetate as eluant gave 64 mg (25%) of an 8:1 mixture of cyclobutane **14** and ene adduct **15**: NMR (CCl_4) (**14**) δ 7.95–7.7 (m, 2), 7.60–7.40 (m, 3), 6.03 (tt, 1, J = 2,2 Hz), 2.89 (d, 2, J = 2 Hz), 2.48 (d, 2, J = 2 Hz), 1.48 (br, 8); NMR (CCl_4) (**15**) δ 7.95–7.7 (m, 2), 7.60–7.40 (m, 3), 5.42 (m, 1), 4.96 (br s, 1), 4.72 (br s, 1), 3.61 (br s, 2), 2.75 (br s, 2), 2.3–1.5 (m, 8); IR (neat) 3070, 2930, 2855, 1660, 1450, 1320, 1145, 1087, 830, 815, 760, 735, 710, 685 cm^{-1}; mass spectrum, m/e 276 (M^+), 141, 135, 134, 125, 119, 115, 107, 106, 105, 97, 93, 83, 91, 81, 79, 78, 77; mol wt calcd for $C_{16}H_{20}SO_2$ 276.1184, found 276.1180.

(12) This experiment was performed by Robert Cordova.

Acknowledgment. We thank David J. Rodini for experimental assistance.

Registry No. **1**, 18913-35-4; **2**, 75232-99-4; **3**, 75233-00-0; **4**, 75281-69-5; **5**, 75281-70-8; **6**, 75281-71-9; **7**, 75233-01-1; **8**, 75233-02-2; **9**, 75233-03-3; **10**, 75233-04-4; **11**, 75233-05-5; (*E*)-**12**, 75233-06-6; (*Z*)-**12**, 75233-07-7; **13**, 2525-42-0; **14**, 75233-08-8; **15**, 75233-09-9; 3-butyn-1-ol, 927-74-2; 3-butynoic acid, 2345-51-9; methyl 3-butynoate, 32804-66-3; 1-hexene, 592-41-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1; 2-ethyl-1-butene, 760-21-4; methylenecyclohexane, 1192-37-6; $EtAlCl_2$, 563-43-9.

Cyclopentene Annulation via Intramolecular Addition of Diazo Ketones to 1,3-Dienes. Applications to the Synthesis of Cyclopentanoid Terpenes

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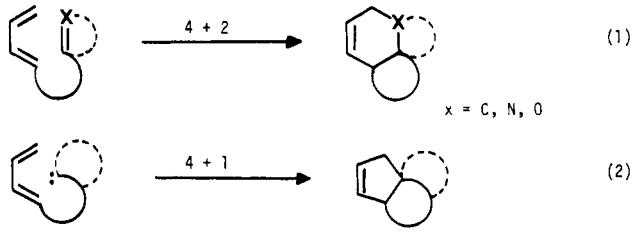
Initial model studies investigating the utility of a new intramolecular cyclopentene annulation procedure are described as pertaining to the preparation of bicyclo[3.3.0]octenones. Several 1-diazo-5,7-octadien-2-ones substituted at the 1-, 7-, or 8-position were decomposed in the presence of $Cu(acac)_2$ to yield stereospecifically the corresponding vinylcyclopropanes **13**, **16**, **21**, **24**, and **27**. The thermal as well as the rhodium-promoted modes of rearrangement to the appropriate cyclopentenes **14**, **17**, **22a,b**, and **28a,b** were studied. Where necessary, diastereomers were separated and structurally assigned by relying on ^{13}C NMR spectroscopy. ^{13}C NMR data are provided for all new compounds in the bicyclooctane series to serve as an aid in assignments of cyclopentanoid terpenes synthesized by this methodology. The intramolecular cyclopropanation–rearrangement sequence of dienic diazo ketones has been shown to provide facile access to bicyclo[3.3.0]octanes of the type **14**, **17**, **22a,b**, and **25a,b** which are of value as terpene synthons. Enhanced stereoselectivity was observed in the rhodium-promoted cyclopentene rearrangements in favor of the less concave diastereomers (**22a**, **25a**, and **28a**). Finally, the sesquiterpene hirsutene (**31**) was synthesized in 37% overall yield by this methodology. ^{13}C NMR data for several tricyclo[6.3.0.$0^{2,6}$]undecane compounds are also provided.

The methodology of simultaneous closure of two rings in an intramolecular fashion has been extensively utilized in the construction of carbocyclic systems. Complex natural products containing an annulated cyclohexene ring have been successfully synthesized by the application of an intramolecular Diels–Alder reaction.[1] Recently, this methodology has entered the alkaloid domain through the use of heteroatom analogues of dienes and dienophiles.[2] Other thermal processes have also been exploited in the context of natural product synthesis particularly where the creation of inaccessible quaternary centers[3] had excluded conventional methods of carbon–carbon bond formation. The ene reactions,[4] the Cope rearrangements, electrocyclic reactions, and their hetereoatom equivalents have all been used in an intramolecular sense.[5]

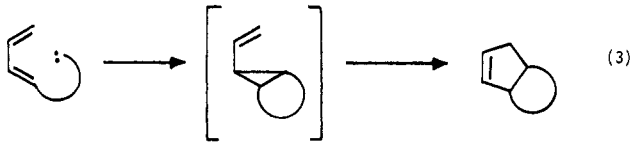
Scheme I



(1)

(2)

Scheme II



(3)

(1) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **16**, 10 (1977); W. Oppolzer, *Synthesis*, 793 (1978); S. R. Wilson and D. T. Mao, *J. Am. Chem. Soc.*, **100**, 6289 (1978); T. Kametani, *J. Chem. Soc., Chem. Commun.*, 16 (1977); S. R. Wilson and D. T. Mao, *J. Org. Chem.*, **44**, 3093 (1979).

(2) B. Nader, R. W. Franck, and S. M. Weinreb, *J. Am. Chem. Soc.*, **102**, 1153 (1980).

(3) S. F. Martin, *Tetrahedron*, **36**, 419 (1980).

0022-3263/80/1945-5020$01.00/0

We sought a method by which a cyclopentene ring could be annulated onto an existing structure, thereby providing a counterpart to [4 + 2] cycloadditions (Scheme I). The presence of functionalized cyclopentane in countless terpenoid natural products further spurred our interest in the development of such a method.

Although chelotropic reactions of carbenes with conjugated dienes (eq 2) have no precedent, it appeared that a two-step sequence could be perfected to provide a synthetically useful equivalent to a 1,4-addition (Scheme II). Furthermore, recent developments in metallocarbene chemistry and in metal-promoted alternatives to thermolytic rearrangements hinted at perhaps achievement of the two-step sequence without the isolation of intermediate vinylcyclopropanes.[6]

We report herein the results of the first major model study directed at establishing the experimental feasibility of this method in organic synthesis.

Since the synthetic compendium of cyclopentanoid chemistry lacks in volume compared to its six-membered cousin, we chose the examination of a bicyclooctane series as the more urgent one. The present study was culminated with the total synthesis of hirsutene (**31**), a sesquiterpene possessing a tricyclo[6.3.0.0^{2,6}]undecane ring system.

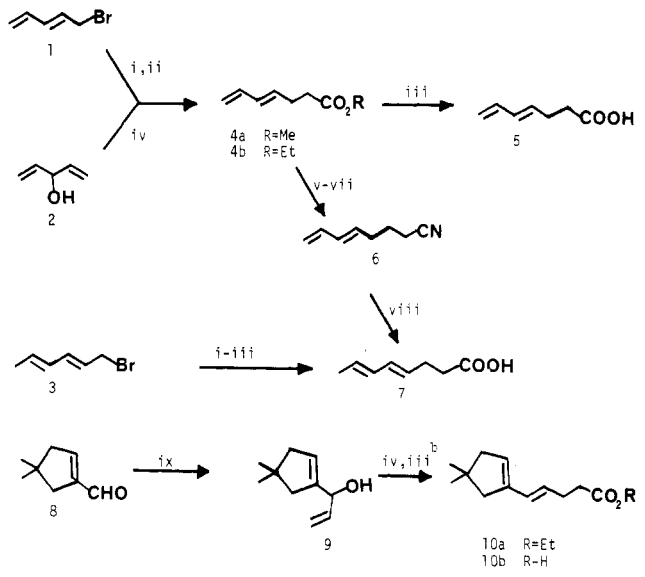
Background

The intramolecular cyclopropanation of olefins is well exemplified in the synthesis of natural products.[7] The mechanistic as well as the stereochemical aspects of carbon–carbon bond formation by this method have been studied,[7,8] and a vast array of experimental conditions for the generation of carbenes and carbenoids is offered through excellent reviews.[9]

By comparison, the internal generation of vinylcyclopropanes by the addition of carbenoids to conjugated dienes is far less common.[10] Examples exist where such vinylcyclopropanes have been exploited in an electrophilic sense as a means of introducing additional substituents.[11]

Correspondingly, the vinylcyclopropane–cyclopentene rearrangement has not enjoyed a widespread appreciation in organic synthesis, although detailed and plentiful mechanistic studies are on hand.[12] The organic chemist has shied away from temperature ranges of 450–600 °C

Scheme III[a]



[a] Reagents: i, $CH_2(CO_2Me)_2$/NaOMe; ii, LiI/DMF/100 °C/1 h; iii, KOH/H_2O; iv, $CH_3C(OEt)_3$/$CH_3CH_2CO_2H$/Δ; v, $LiAlH_4$; vi, MsCl/Et_3N then LiBr/acetone; vii, NaCN/DMF; viii, *p*-TsOH/benzene/Δ; ix, CH_2=CHMgBr/THF. [b] Note: the use of $Hg(OAc)_2$ gave mixtures of regioisomers; the use of propionic acid alone gave low yields, due to the loss of catalyst (~145 °C, reflux); a single isomer was thus obtained in high yield by using in situ generated $Hg(O_2CCH_2CH_3)_2$.

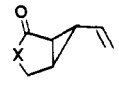
which are necessary to bring about this conversion. Although such pyrolyses become impractical, especially with polyfunctional molecules, they are frequently carried out on simple systems with reliable results and in high yields.[13] Quite recently a method has been reported for oxycyclopropane–cyclopentenol rearrangement which takes place at ambient temperature.[14]

We envision the application of thermolytic cyclopentene rearrangement only as means for the construction of basic skeletons of low molecular weight (<200) substances. Other methods of this rearrangement would then be used on substrates of greater complexity.

Results and Discussion

Three crucial factors control the utility of intramolecular cyclopentene annulation: (a) ring-size limit in cyclopropanation closures, (b) preparation of dienic acids, and (c) methods of rearrangement.

Earlier we have reported on the production of bicyclo[*n*.1.0] ketones of the general type **11** in high yields through



11 X = $(CH_2)_{n-2}$

the copper-catalyzed decomposition of the corresponding diazo ketones.[15] The steric course of these closures paralleled that previously reported for simple olefinic cyclopropanations.[15,16] Only closures of five- and six-membered

(4) W. Oppolzer and V. Snieckus, *Angew. Chem., Int. Ed. Engl.*, **17**, 476 (1978); J. M. Conia and P. LePerchec, *Synthesis*, 1 (1975).

(5) For reviews and recent applications of these rearrangements, see: S. J. Rhodes and N. R. Raulins, *Org. React.*, **22**, 1 (1975); F. E. Ziegler, *Acc. Chem. Res.*, **10**, 227 (1977); P. S. Mariano, D. Dunaway-Mariano, and P. L. Huesmann, *J. Org. Chem.*, **44**, 124 (1979); P. A. Bartlett and W. F. Hahne, *ibid.*, **44**, 882 (1979).

(6) M. Murakami and S. Nishida, *Chem. Lett.*, 927 (1979); V. Aris, J. M. Brown, J. A. Coneely, B. T. Golding, and P. H. Williamson, *J. Chem. Soc., Perkin Trans. 2*, 4 (1975); J. M. Brown, et al., *ibid.*, 962 (1979).

(7) For reviews see: C. H. Heathcock, "Total Synthesis of Natural Products", Vol. 2, Wiley-Interscience, New York, 1973, p 197; S. D. Burke and P. A. Grieco, *Org. React.*, **26**, 361 (1979).

(8) See for example: W. Kirmse and D. Grassman, *Chem. Ber.*, **99**, 1746 (1966); M. M. Fawzi and C. D. Gutsche, *J. Org. Chem.*, **31**, 1390 (1966); W. Kirmse, Ed., "Carbene Chemistry", Academic Press, New York, 1971; D. S. Wulfman, et al., *Tetrahedron*, **32**, 1231, 1241, 1251, 1257 (1976).

(9) E. Wenkert, *Acc. Chem. Res.*, 13, 27 (1980); S. D. Burke and P. A. Grieco, *Org. React.*, 26, 361 (1979).

(10) See for example: M. N. Nwaji and O. S. Onyiriuka, *Tetrahedron Lett.*, 2255 (1976); W. von Doering, et al., *Tetrahedron*, **21**, 25 (1965); **23**, 3943 (1967); K. Kondo, et al., *Tetrahedron Lett.*, 113 (1977); K. Kondo, P. Unemoto, K. Yako, and D. Tunemoto, *ibid.*, 3927 (1978); D. F. Taber, *J. Am. Chem. Soc.*, **99**, 3513 (1977); T. Hudlicky, J. P. Sheth, V. Gee, and D. Barnvos, *Tetrahedron Lett.*, 4889 (1979).

(11) S. Danishefsky, R. McKee, and R. K. Singh, *J. Am. Chem. Soc.*, **99**, 4783 (1977); J. D. White, S. Torii, and J. Mogami, *Tetrahedron Lett.*, 2879 (1974); ref 10.

(12) See for example: H. M. Frey and R. Walsh, *Chem. Rev.*, **68**, 103 (1968); H. G. Richey, Jr., and D. W. Shull, *Tetrahedron Lett.*, 575 (1976).

(13) C. Melchiore, *Synth. Commun.*, **6**, 125 (1976); B. M. Trost and M. J. Bogdanowitz, *J. Am. Chem. Soc.*, **95**, 5298, 5307, 5311 (1973).

(14) R. L. Danheiser, C. Martinez-Darilla, and J. M. Morin, Jr., *J. Org. Chem.*, **45**, 1340 (1980); ref 12.

(15) T. Hudlicky, J. P. Sheth, V. Gee, and D. Barnvos, *Tetrahedron Lett.*, 4889 (1979).

(16) B. M. Trost, D. F. Taber, and J. B. Alper, *Tetrahedron Lett.*, 3857 (1976); ref 11.

rings prove synthetically useful, a result also endorsed by investigators of olefinic closures.[17]

The dienic acids necessary for the preparation of diazo ketones are available via several routes. We have used the Arndt–Eistert reaction to homologize heptadienoic acid **5** (Scheme III) with good results;[18] however, the frequent exposure of the research personnel to diazomethane makes this method somewhat less desirable. Heptadienoic acid **5** can be obtained via malonic ester synthesis from pentadienyl bromide **1** or by ortho ester Claisen rearrangement of carbinol **2**,[19] the latter procedure being superior in yields to any other method investigated.

The octadienoic acid **7** is accessible from the known sorbyl bromide **3** via malonic ester synthesis. We also obtained **7** from heptadienoate **4** via a reduction–bromination–cyanide displacement–isomerization sequence which yielded nitrile **6**. However, this compound was contaminated with the *Z* isomer and was not suited for our study.

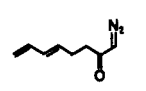
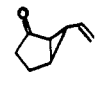
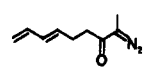
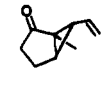
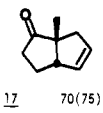
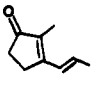
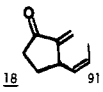
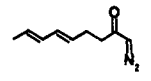
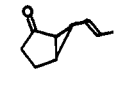
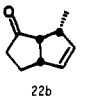
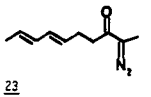
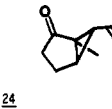
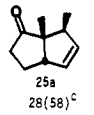
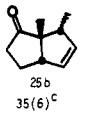
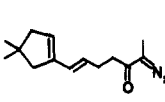
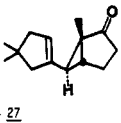
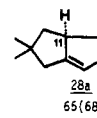
The ortho-Claisen rearrangement of substituted carbinols of the type **9** has been studied by Cresson et al.[21] with respect to regiochemistry. Some selectivity in favor of the less substituted olefin was observed. This selectivity proved even more pronounced when one of the double bonds was contained in a ring. In the case of acid **10** an overall yield of 82% was achieved for the two-step sequence by using in situ generated mercuric propionate (10 mol %) in triethyl orthoacetate as a reagent and a solvent. The acids (via their chlorides) were converted into diazo ketones by the use of etheral diazomethane or diazoethane.[22] In order to obtain all of their spectral data, the diazo ketones were purified by rapid column chromatography. Although they decomposed on standing at room temperature (>48 h) they could be kept indefinitely under nitrogen and below −10 °C.

The cyclopropanes **13**, **16**, **21**, **24**, and **27** were generated by refluxing dilute solutions of **12**, **15**, **20**, **23**, and **26** in benzene containing 10 mol % of $Cu(acac)_2$. In each case a single stereoisomer was formed in high yield (>90%) as evidenced by spectral analysis. Again, this observation directly parallels the stereospecificity recorded in the various olefinic cyclopropanations.[15,16]

With the vinylcyclopropanes on hand, the study entered its key point. The substitution patterns of bicyclooctanes **14**, **17**, **22a,b**, and **25a,b** were chosen for their resemblance to structural subunits of various sesquiterpenes (coriollins, acoranes, cedranes, etc.).[23] It appeared that the successful application of this methodology to the synthesis of the above terpenes depended to a greater extent on the actual yield of the rearrangement step than on the stereochemical outcome. The C-8 center would be controlled by a isomerization–hydrogeneration sequence,[24,25] and the ring junction stereochemistry (under the conditions of the rearrangement) would yield the cis-fused ring system. The presence of an acyl group on the cyclopropane ring eliminated the frequently encountered problems of regiochemistry during the pyrolyses of simple alkylcyclopropanes by regioselectively activating the ring toward a biradical cleavage. The anticipated production of stereoisomers thus became useful only in providing exact ^{13}C NMR data for any future comparisons.[26]

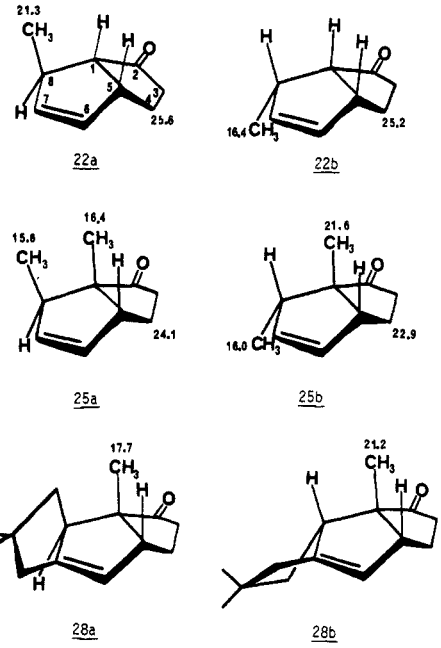
The problems associated with 1,5 hydrogen shift of *cis*-vinylalkylcyclopropanes competing with cyclopentene

Table I

diazo ketone	cyclopropane, % yield[a]	bicyclooctane, % yield, conditions
 12	 13 95	 14 65(70)[b] 600°, Vycor
 15	 16 94	 17 70(75)  19 25 600°C, Vycor
		 18 91 400°C, Pyrex
 20	 21 82	 22a 18(62)[c]  22b 48(5)[c] 600°C, Vycor
 23	 24 75	 25a 28(58)[c]  25b 35(6)[c] 600°C, Vycor
 26	 27 94	 + 11β-epimer 28a 65(68) 28b 10(0)

[a] Isolated yields. [b] Numbers in parentheses represent the yields of rhodium-promoted rearrangements. [c] Estimated by GC (Carbowax 1500).

Chart I



(17) G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961); also ref 8.
(18) T. Hudlicky and J. P. Sheth, *Tetrahedron Lett.*, 2667 (1979).
(19) W. Oppolzer and R. Hunadi, unpublished results.
(20) K. Mori, *Tetrahedron*, **30**, 3807 (1974).
(21) S. Bangel and P. Cresson, *C. R. Hebd. Seances Acad. Sci.*, **268**, 1535 (1969).
(22) J. A. Marshall and J. J. Partridge, *J. Org. Chem.*, **33**, 4094 (1968).
(23) T. K. Devon and A. I. Scott, "Handbook of Naturally Occurring Compounds", Vol. 2, Academic Press, New York, 1972.
(24) See for example: S. Danishefsky, H. Hirama, K. Gombatz, T. Harayama, E. Berman, and P. Schuda, *J. Am. Chem. Soc.*, **100**, 6356 (1978); J. J. Beereboom, *J. Org. Chem.*, **30**, 4230 (1965).
(25) E. Piers and K. F. Cheng, *Chem. Commun.*, 562 (1969).
(26) The ^{13}C NMR data concerning models for the assignment of cyclopentanoid terpenes are rare; see ref 32–35.

Table II. Rearrangement of 27

reagent	temp, °C	proportion of 28a/28b	total yield, %
Vycor/$PbCO_3$	500	2/3	50
	540	2/3	62
	560	1/1	70
	580	3/1	75
	590	6/1	75
$(C_2H_4)_2Rh(acac)$	80	90/10	40
	110	95/5	65
	140	95/5	70
	180	100/0	68

rearrangement have been solved by carefully monitoring the temperature during the pyrolysis of cyclopropane **16**. Our results indicated selectivity in the preparation of either enone **18** or bicyclooctane **17**.[27]

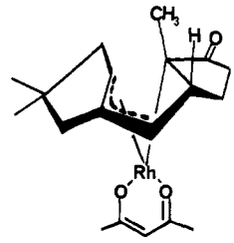
The pyrolyses were carried out by flash evaporation of samples through a properly conditioned (see Experimental Section) Vycor tube at reduced pressure. The contact time in all cases was approximately 2 min, and the recovery of crude condensates was excellent (>95%). In this fashion, bicyclooctanes **14**, **17**, **22a,b**, **25a,b**[28] and **28a,b** were obtained. The results of our study are summarized in Table I.

It was possible in most cases to separate the diastereomers by careful medium-pressure liquid chromatography. A 1:2 mixture of **22a** and **22b** was obtained from cyclopropane **21**, and a 1:1 composition of ketones **25a** and **25b** was observed in the case of its angularly methylated analogue **24** (see Chart I).

The composition of these mixtures is best understood on examination of molecular models. The nonbonded interactions of the C-8 methyl group with the bridgehead hydrogens create a steric congestion not existing in the all-cis system of **22b**. Under the conditions of the rearrangement the less crowded pattern of **22b** predominates. The steric crowding becomes more pronounced upon the introduction of an angular methyl group in **25a** and **25b**. On the basis of the above reasoning an increased proportion of **25b** was expected; however, a mixture of similar composition to that of **22a,b** was obtained. One possible explanation, supported in part by the ^{13}C NMR shifts (see below), would be in the increased rigidity of a system such as **25**. The C-8 methyl in **25b** experiences new interactions with the C-4 methylene and the carbonyl group. These interactions begin to compare favorably with the hindrance experienced by the cis-oriented methyls in **25a**, the result manifesting itself in only a 1:1 mixture of **25a** and **25b**.

The rearrangement of hirsutene precursor **27** proved to be more sensitive as slight variations in the pyrolytic conditions altered the ratio of diastereomers **28a** and **28b**. The cis,anti,cis-fused tricycloundecane ring system should be marginally more stable than the corresponding cis,-syn,cis epimer **28b**. In the thermolyses of **27**, **28a** thus predominated by a ratio of 6:1 at higher temperatures.

Enhanced stereoselectivity was observed in the rhodium-promoted bond reorganization of **27** (Table II). The almost complete absence of the cis,syn,cis-fused epimer **28b** in these rearrangements hints at the effective *concavity* of an intermediate of the type **29** as the determinant



29

of the final stereochemical outcome. The initial complexation of $(C_2H_4)_2Rh(acac)$ with **27** may be followed by a number of transformations preceding the ring closure of complex **29**. The investigators of rhodium-promoted cyclopentene rearrangement of $(C_2H_4)_2Rh(acac)$[6,29] or bis-(1,5-cyclooctadienyl)nickel[6] pointed out the probability of a *concerted* $[2_{\pi_s} + 2_{\sigma_s}]$ opening of vinylcyclopropane which can evenutally lead to a structure such as **29** prior to an envisioned $[2_{\pi_s} + 2_{\sigma_s}]$ ring closure to cyclopentene. Since it seems likely that such closure takes place from **29**, the presence of a bulky acetoacetonate ligand may prevent the system from reaching the more concave geometry which would favor the formation of cis,syn,cis-fused tricyclopentanoid **28b**.

Similarly, the rhodium-promoted rearrangements of **21** and **24** produced mixtures in which the *less concave epimer* predominated (Table I).

In this fashion some degree of control has been introduced regarding the stereochemical outcome at C-8 of substituted bicyclooctanes. These results become valuable in the context of the anticipated roles of compounds **22**, **25**, and the like as synthons for the preparation of aforementioned terpenoids. However, the necessity for stoichiometric amounts of rather costly $(C_2H_4)_2Rh(acac)$ precludes for the moment any practical use of this method on a large scale, until a procedure for the recovery of rhodium is perfected or until a system is discovered which operates in a catalytic mode.[6]

Detailed ^{13}C NMR analysis was used to assign the relative stereochemistry in substituted bicyclooctanes (Chart I). The distinguishing features in the ^{13}C NMR spectra of **22a** and **22b** were the chemical shifts of C-8 methyl groups. The aforementioned 1,3-nonbonded interactions of C-8 and C-4 in **22b** manifested themselves in an upfield shift of 4.9 ppm relative to that of **22a** as a result of shielding of the C-8 methyl.[30] The C-8 methyl in **22b** is in the proximity of the carbonyl group and would be expected to be deshielded in comparison with the C-8 methyl in **22a**; however, the magnitude of the effect of the carbonyl on the ^{13}C chemical shift is small compared to the γ effect.[31] The angular methyl group in **25a** is shielded to the extent of 5.2 ppm. Likewise, the C-8 methyl normally found around 21 ppm in similar systems[32] resonates 5.7 ppm upfield of its counterpart in **22a**. These assignments

(27) For the results of this study and a compilation of references pertaining to the [1,5] shift of *cis*-alkylvinylcyclopropanes, see T. Hudlicky and F. J. Koszyk, *Tetrahedron Lett.*, 2487 (1980).

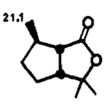
(28) The bicyclooctanes of lower molecular weight were extremely volatile. Freeze-drying techniques or spinning-band columns had to be employed during the removal of solvents to avoid significant losses of materials.

(29) See also R. G. Solomon, M. F. Solomon, and J. L. C. Kachinski, *J. Am. Chem. Soc.*, **99**, 1043 (1977).

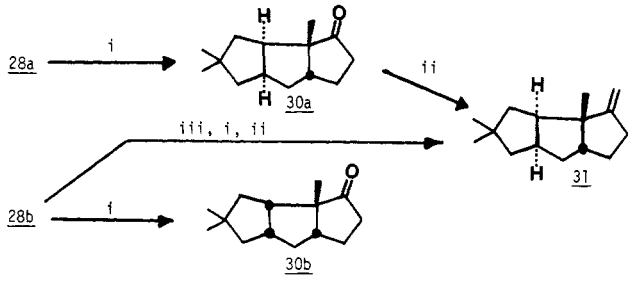
(30) See for example: G. G. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972; also ref 33–35.

(31) F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden, London, 1978.

(32) We have used the pulegonic acid lactone as our model in ^{13}C NMR assignments. Preparation of this lactone and its α-epimer and the ^1H NMR stereochemical assignment have been reported: J. Wolinsky, H. Wolf, and T. Gibson, *J. Org. Chem.*, **28**, 274 (1963).



Scheme IV[a]



[a] i, H_2/Pd(C); ii, $(Ph)_3P{=}CH_2$/Me_2SO; iii, $RhCl_3$/EtOH/H_2O or *p*-TSOH/toluene/Δ.

are somewhat in accord with a recent compilation of ^{13}C NMR parameters of diversely substituted bicyclo[3.3.0]-octanes.[33]

Careful separation of the stereoisomers **28a** and **28b** and determination of their ^{13}C NMR spectra revealed a corresponding upfield shift of 3.5 ppm for the angular methyl in **28a**. This assignment compared favorably with the known chemical shifts for hirsutic acid[34] and other tricyclo[6.3.0.$0^{2,6}$]undecane systems.[35]

The final proof of stereochemistry was obtained by hydrogenation of **28a** and **28b** to saturated ketones **30a** and **30b**, respectively. Only **30a** had an IR spectrum identical with the known degradation product of hirsutene **31**[36] (Scheme IV). We have already reported on the total synthesis of hirsutene by the above route in which **28b** was also convertible to **30a** via an isomerization–hydrogenation sequence.[37]

Conclusions

The above study points out the general utility of the two-step sequence in cyclopentene annulation. The pyrolytic conditions for the cyclopentene rearrangement gave good results with compounds of lower molecular weight. Larger or more complex molecules can be successfully rearranged by the use of $(C_2H_4)_2Rh(acac)$ in toluene. This method is inferior to pyrolytic conditions in cases where the high volatility of products renders their recovery from solvents difficult.

The use of ethyl diazo ketones and the previously reported selectivity in 1,5 hydrogen shift vs. cyclopentene rearrangement become a useful route to angularly methylated ketones of the type **25**. An entry to linearly fused cyclopentanoids as well as [6.3.0.$0^{4,8}$]undecane systems[38] can be gained from compounds of types **21** and **24**. Acoranes, cedranes, and pentalenolactones should be accessible via the methodology which leads to ketones **22**, especially in view of the successful differentiation in the conditions of rearrangement to produce either **22a** or **22b** as the major products.

Further endeavors include the following: (a) identical study in a bicyclo[4.3.0]nonane series; (b) exploitation of the retroene product **18** in the syntheses of functionalized cyclopentanes; (c) development of the conditions for the in situ rearrangements involving $(C_2H_4)_2Rh(acac)$ with the emphasis on feasible recovery of the catalyst; (d) acid-catalyzed closures of dienic diazo ketones as the most direct means of accomplishing the intramolecular cyclopentene annulation; (e) syntheses of other cyclopentanoid natural products by this methodology.

Experimental Section

Melting and boiling points are uncorrected. Melting points were determined on a Mel-Temp apparatus. ^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 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 or on a Perkin-Elmer Model 257 infrared spectrophotometer. Mass spectra were obtained on a Du Pont 20-491 instrument (low resolution) or on a double-focusing (high resolution) Du Pont 21-110C instrument.

Tetrahydrofuran was freshly distilled before use from potassium and benzophenone. Anhydrous ethyl ether was Mallinckrodt reagent grade and was used without further purification. Medium-pressure liquid chromatography was performed by using E. Merck silica gel columns. Column chromatography was performed by using Macherey Nagle and Co. silica gel 60 (70–270 mesh) or J. T. Baker 1-0540 alumina. All nonhydrolytic reactions were performed under a nitrogen atmosphere.

4,6-Heptadienoic Acid (5). (A) Ortho Claisen Method. A solution of ethyl formate in 150 mL of dry tetrahydrofuran (65 g, 0.9 mol) was added to cooled solution of vinylmagnesium bromide (from 280 g of vinyl bromide and 58 g (2.4 mol) of magnesium turnings) while the temperatures were kept below 30 °C. After being stirred overnight at room temperature, the reaction was quenched with 3 N hydrochloric acid and extracted with ether. The organic layers were dried and distilled through a Vigreux column at a 65 °C take-off temperature, leaving a solution of **2** suitable for the next step. To this solution were added benzene (600 mL), triethyl orthoacetate (708 g, 4.4 mol), and propionic acid (2.5 mL). The mixture was refluxed for 16 h, the solvents were removed by distillation, and the remainder was fractionated at reduced pressure to give heptadienoate **4b**, bp 40–55 °C (0.5 mm). The ester was hydrolyzed (25% potassium hydroxide/methanol, reflux, 2 h) directly to give 39.3 g (86%, 35% from ethyl formate) of acid **5**: bp 68–70 °C (1.2 mm); IR (neat) 3070, 1702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2–2.5 (m, 4 H), 4.8–6.5 (m, 5 H), 11.9 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.4 (t), 33.7 (t), 115.9 (t), 132.2 (d), 132.3 (d), 136.8 (d), 179.8 (s); mass spectrum (70 eV), *m/e* (relative intensity) 126 (M^+, 75), 81 (B, 100), 86 (25), 84 (43), 80 (55), 67 (74); calcd for $C_7H_{10}O_2$ *m/e* 126.0681, found *m/e* 126.0682.

(B) Malonic Acid Synthesis Method. Pentadienyl bromide, **1**[20] (10.0 g, 0.068 mol), was added to a solution of sodiomalonate [from 8.98 g (0.068 mol) of dimethyl malonate and 1.6 g (0.068 mol) of sodium metal] in methanol. After being refluxed overnight, the mixture was quenched with brine and extracted with ether, giving, after evaporation, 11.8 g (83%) of crude diester. This material was hydrolyzed (25% potassium hydroxide, reflux, 2 h) to give 9.02 g (94%) of the corresponding diacid, which was refluxed in dry dimethyl formamide (200 mL) for 1 h. The mixture was diluted with water, acidified, and extracted with ether. The combined etheral layers were rinsed with water (5 × 100 mL), dried, and evaporated to give 4.68 g (70%) of acid **5** (54% from **1**).

4,5-Octadienoic Acid (7). Sorbyl bromide **3**[20] (6.36 g, 0.040 mol) was added to a suspension of sodiomalonate in methanol [from 5.2 g (0.040 mol) of dimethyl malonate and 0.91 g of sodium]. The mixture was refluxed for 12 h to afford on workup 7.22 g (86%) of diester. This material was hydrolyzed and decarboxylated as described above to give 4.39 g (56% from **3**) of acid **7**: mp 44–45 °C; IR (neat) 3100, 1709 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7 (d, 3 H, *J* = 7 Hz), 2.2–2.5 (m, 4 H), 4.8–6.3 (m, 4 H), 11.9 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.0 (q), 27.6 (t), 34.0 (t), 127.8 (d), 128.8 (d), 131.6 (d), 131.8 (d), 179.8 (s); mass spectrum (70 eV), *m/e* (relative intensity) 140 (M^+, 50), 95 (24), 81 (B, 100), 79 (98), 67 (32), 53 (45), 41 (50), 28 (50); calcd for $C_8H_{12}O_2$ *m/e* 140.0837, found *m/e* 140.0842.

(33) J. K. Whitesell and R. S. Matthews, *J. Org. Chem.*, **42**, 3878 (1977).
(34) G. Mellows and T. C. Feline, *J. Chem. Soc., Chem. Commun.*, 63 (1974).
(35) M. G. Venegas and R. D. Little, *Tetrahedron Lett.*, 309 (1979).
(36) See K. Tatsuta, K. Akimoto, and M. Kinoshita, *J. Am. Chem. Soc.*, **101**, 6116 (1979), and the references within.
(37) T. Hudlicky, T. Kutchan, S. R. Wilson, and D. T. Mao, *J. Am. Chem. Soc.*, **102**, 6351 (1980).
(38) For compilations of cyclopentanoid terpenes of recent interest, see: W. Oppolzer, K. Battig, and T. Hudlicky, *Helv. Chim. Acta*, **62**, 1493 (1979); ref 24; M. Kaneda, et al., *Tetrahedron Lett.*, 4609 (1972).

1-(3,3-Dimethylcyclopent-1-enyl)-1-hydroxy-2-propene (9). A solution of 5,5-dimethyl-*cis*-2,3-epoxycyclohexanol[39] (14.2 g, 0.1 mol) in 50 mL of dry toluene was added to a stirred, refluxing mixture of hexamethylphosphoramide (32.6 g, 0.2 m), 17.4 g of anhydrous lithium bromide, and 100 mL of dry toluene over 30 min. After 5 min of additional heating, the reaction mixture was cooled and diluted with 300 mL of ether. The LiBr·HMPA complex was separated, and the etheral solution washed with water (5 × 50 mL). Filtration through a short silica gel column and evaporation at reduced pressure (no heating!) gave aldehyde 8 (approximately a 50% solution in toluene). This solution was added at 0 °C to 1.4 mol of vinylmagnesium bromide (from 15 g of vinyl bromide and 3.5 g of magnesium turnings) in 100 mL of tetrahydrofuran. The reaction was stirred for 1 h at 0 °C and then at room temperature for 2 h more. Following quenching of the reaction with saturated ammonium chloride solution and extraction with ether, the crude oil obtained after evaporation was distilled to give 13.7 g (90.1%) of **9**: bp 61 °C (2 mm Hg); IR (neat) 3350, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 6 H), 2.1 (br s, 4 H), 3.4 (s, 1 H, hydroxyl), 4.5 (d, 1 H, J = 6 Hz), 5.0–5.9 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 29.8 (q, 2 methyl groups), 38.4 (t), 47.5 (t), 48.4 (s), 72.4 (d), 114.7 (t), 124.0 (d), 139.2 (d), 144.2 (s); mass spectrum (70 eV), m/e (relative intensity) 152 (M^+, 15), 137 (22), 119 (20), 109 (25), 97 (50), 95 (B, 100), 91 (40), 83 (40), 67 (35); calcd for $C_{10}H_{16}O$ m/e 152.1201, found m/e 152.1206.

4-(3,3-Dimethylcyclopent-1-enyl)-4-pentenoic Acid (10b). A solution of carbinol **9** (10 g, 0.066 mol) in 250 mL of triethyl orthoacetate containing 900 mg of propionic acid and 400 mg of mercuric acetate was refluxed under nitrogen for 16 h. The reaction mixture was cooled, diluted with ether (250 mL), and washed with 3 N hydrochloric acid (2 × 240 mL). Evaporation gave crude ethyl ester **10a**: oil; IR (neat) 1736, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 6 H), 1.15 (t, 3 H, J = 7 Hz), 2.2 (m, 4 H), 2.4 (br s, 4 H), 4.1 (q, 2 H, J = 7 Hz), 5.4 (br s, 2 H), 6.25 (d, 1 H, J = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 14.3 (q), 28.1 (t), 30.0 (q, 2 methyl groups), 34.1 (t), 34.2 (t), 38.2 (s), 47.9 (t), 48.0 (t), 127.7 (d), 128.1 (d), 128.5 (d), 140.9 (s), 172.9 (s); mass spectrum (70 eV), m/e (relative intensity) 222 (M^+, 6), 207 (12), 133 (40), 119 (60), 105 (35), 91 (65), 79 (35); calcd for $C_{14}H_{22}O_2$ m/e 22.1620, found m/e 222.1624. Crude **10a** was dissolved in 20 mL of ethanol, and the mixture was added to 150 mL of 20% aqueous potassium hydroxide and refluxed for 2 h. The cooled mixture was washed with hexane (2 × 50 mL) and hexane–ether (2:1; 1 × 50 mL), and the aqueous layer was acidified and extracted with chloroform. The crude product was distilled [100–115 °C (0.10 mm), Kugelrohr] to give 10.3 g (82%) of **10b** as an oily solid: IR (neat) 3200–2800, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 6 H), 2.1 (br s, 4 H), 2.4 (br s, 4 H), 5.6 (s, 1 H), 5.65 (br s, 1 H), 6.38 (d, 1 H, J = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 27.8 (t), 30.1 (q) (2 methyl groups), 34.0 (t), 38.3 (s), 48.0 (t), 48.6 (t), 127.7 (d), 128.0 (d), 128.7 (d), 140.9 (s), 179.9 (s); mass spectrum (70 eV), m/e (relative intensity) 194 (M^+, 5), 149 (22), 138 (20), 135 (18), 125 (50), 107 (49), 91 (40), 79 (38), 55 (B, 60); calcd for $C_{12}H_{18}O_2$ m/e 194.1307, found m/e 194.1313.

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.

4,6-Heptadienoyl chloride: yield 83%; bp 32–34 °C (0.2 mm); IR (neat) 1793 cm^{-1}.

4,5-Octadienoyl chloride: yield 84%; bp 70 °C (bath temperature; 1 mm); IR (neat) 1793 cm^{-1}.

4-(3,3-Dimethylcyclopent-1-enyl)-4-pentenoyl chloride: bp 80–85 °C (0.05 mm, Kugelrohr); IR (neat) 1780 cm^{-1}.

Preparation of Diazo Ketones. The appropriate acid chloride was added dropwise to an ethereal solution of diazomethane[40] or diazoethane[40] at 0 °C. The solution was permitted to stand for 0.5 h, was boiled briefly to expel excess diazoalkane, and was evaporated to give pure diazo ketones as pale yellow oils. If the corresponding esters were the contaminants, analytically pure diazo ketones were obtained from rapidly performed chromatography on silica gel (CH_2Cl_2).

1-Diazo-5,7-octadien-2-one (12): yield 100%; IR (neat) 2092, 1633 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2–2.5 (m, 4 H), 4.8–6.4 (m, 5 H), 5.2 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.2 (t), 38.4 (t), 51.6 (d), 115.7 (t), 132.1 (d), 132.7 (d), 136.8 (d), 194.9 (s); calcd for $C_8H_{10}N_2O$ m/e 150.0793, found m/e 150.0791.

1-Diazo-5,7-nonadien-2-one (20): yield 98%; IR (neat) 2105, 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (d, 3 H, J = 6 Hz), 2.2–2.5 (m, 4 H), 5.3 (s, 1 H), 4.8–6.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 17.5 (q), 27.9 (t), 40.3 (t), 54.5 (d), 127.8 (d), 129.3 (d), 131.4 (d), 131.6 (d), 194.2 (s); calcd for $C_9H_{12}N_2O$ m/e 164.0950, found m/e 164.0947.

2-Diazo-6,8-nonadien-3-one (15): yield 96%; IR (neat) 2070, 1636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9 (s, 3 H), 2.1–2.8 (m, 4 H), 4.8–6.6 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 8.2 (q), 27.5 (t), 37.2 (t), 62.1 (s), 115.6 (t), 132.1 (d), 132.8 (d), 136.0 (d), 193.8 (s); calcd for $C_9H_{12}N_2O$ m/e 164.0949, found m/e 164.0953.

2-Diazo-6,8-decadien-3-one (23): yield 99%; IR (neat) 2081, 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.85 (d, 3 H, J = 6 Hz), 2.10 (s, 3 H), 2.3–2.7 (m, 4 H), 4.9–6.4 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 8.1 (q), 17.9 (q), 27.6 (t), 37.5 (t), 58.4 (s), 127.5 (d), 129.3 (d), 129.5 (d), 131.5 (d), 193.2 (s); calcd for $C_{10}H_{14}N_2O$ m/e 178.1106, found m/e 178.1108.

1-(3,3-Dimethylcyclopent-1-enyl)-6-diazohex-1-en-5-one (26). Acid **10b** (0.5 g, 0.0025 mol) was refluxed in 22 mL of a 2:1 mixture of hexane/oxalyl chloride for 1 h. Excess solvent and oxalyl chloride were removed in vacuo, and the oil was distilled [85–90 °C (0.1 mm), Kugelrohr] to give acid chloride (IR 1800 cm^{-1}). The *neat*[41] acid chloride was slowly added to *10 mL* of ethereal diazoethane solution (from 1.06 g nitrosoethylurea) at 0 °C. After the mixture was allowed to stand at room temperature for 1 h, the solvent was removed to give 580 mg (95.4%) of pure diazo ketone **26**: IR (neat) 2060, 1640, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 6 H), 2.08 (s, 3 H), 2.4 (br s, 4 H), 2.7 (br s, 4 H), 4.6 (br s, 1 H), 5.65 (s, 1 H), 6.35 (d, 1 H, J = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 8.2 (q), 27.8 (t), 30.0 (q) (2 methyl groups), 37.6 (t), 38.2 (s), 46.5 (t), 47.9 (t), 61.9 (s), 127.8 (d), 128.3 (d), 128.5 (d), 140.9 (s), 193.6 (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 12–18 h. After removal of the solvent, the residue was filtered through alumina, eluting with methylene chloride or ether. Solvent was removed, and the crude product was distilled, giving the vinylcyclopropane as a colorless oil.

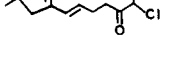
6β-Ethenyl-1,5β-bicyclo[3.1.0]hexan-2-one (13): yield 95%; bp 50 °C (bath temperature; 0.5 mm); IR (neat) 1723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8 (m, 1 H), 1.88 (m, 1 H), 1.7–2.2 (m, 5 H), 4.8–5.5 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 22.7 (t), 28.9 (d), 30.2 (d), 32.3 (t), 35.9 (d), 114.5 (t), 136.4 (d), 212.1 (s); mass spectrum (70 eV), m/e (relative intensity) 122 (M^+, 37), 78 (B, 100), 66 (93), 53 (64), 39 (77); calcd for $C_8H_{10}O$ m/e 122.0732, found m/e 122.0733.

1β-Methyl-6β-ethenylbicyclo[3.1.0[hexan-2-one (16): yield 94%; bp 62.5 °C (0.4 mm); IR (neat) 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (s, 3 H), 1.9 (m, 2 H), 2.1 (m, 4 H), 4.9–5.6 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 9.5 (q), 21.8 (q), 32.2 (t), 33.2 (d), 34.2 (d), 38.6 (s), 116.9

(39) G. Magnusson and S. Thoren, *J. Org. Chem.*, 38, 1380 (1973).

(40) The following procedure was used to generate diazoalkanes: 0.5 g of nitrosoalkylurea (~0.004 mol) was added in portions at 0 °C to an Erlenmeyer flask containing 1.5 mL of 50% potassium hydroxide and 6 mL of ethyl ether. The two-phase system was either swirled or stirred. The ethereal layer was decanted, dried over KOH pellets, and decanted. Such solutions were suitable for 0.001 mol of an acid chloride.

(41) It proved essential to add *neat* acid chloride to a 0.1 M solution of diazoethane. Any deviation from this concentration led to an almost quantitative production of α-chloro ketone: IR (neat) 1712, 1640, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 6 H), 1.62 (d, 3 H, J = 7 Hz), 2.3 (s, 2 H), 2.4 (q, 2 H, J = 6 Hz), 2.9 (m, 4 H), 4.4 (q, 1 H, J = 7 Hz), 5.4 (br s, 2 H), 6.3 (d, 1 H, J = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 20.0 (q), 26.8 (t), 30.2 (q, 2 methyl groups), 38.1 (t), 38.9 (s), 46.5 (t), 47.9 (t), 58.5 (d), 127.8 (d), 128.0 (d), 128.6 (d), 140.8 (s), 204.6 (s); mass spectrum (70 eV), m/e (relative intensity) 240 (M^+, 25), 225 (25), 149 (37), 134 (75), 118 (B, 100), 93 (65), 91 (82), 79 (62), 63 (60), 55 (37). Anal. Calcd for $C_{14}H_{21}OCl$: m/e 240.1281. Found: m/e 240.1287.



(t), 134.3 (d), 215.0 (s); mass spectrum (70 eV), *m/e* (relative intensity) 136 (M^+, 32), 93 (52), 79 (B, 100); calcd for $C_9H_{12}O$ *m/e* 136.0888, found *m/e* 136.0886.

6β-(1-Prop-1-enyl)-1,5β-bicyclo[3.1.0]hexan-2-one (21): yield 82%; IR (neat) 1724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (m, 1 H), 1.6 (d, 3 H, *J* = 6 Hz), 1.8–2.1 (m, 6 H), 4.8–5.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.8 (q), 22.9 (t), 28.9 (d), 29.7 (d), 32.4 (t), 36.1 (d), 125.4 (d), 129.9 (d) 212.9 (s); mass spectrum (70 eV), *m/e* (relative intensity) 136 (M^+, 8), 121 (7), 94 (76), 84 (38), 79 (B, 100), 53 (12), 39 (24); calcd for $C_9H_{12}O$ *m/e* 136.0888, found *m/e* 136.0890.

1β-Methyl-6β-(1-prop-1-enyl)bicyclo[3.1.0]hexan-2-one (24): yield 75%; IR (neat) 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (s, 3 H), 1.2 (m, 1 H), 1.7 (d, 3 H, *J* = 6 Hz), 1.8–2.1 (m, 5 H), 5.0–5.8 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.5 (q), 18.1 (q), 22.0 (t), 32.4 (t), 32.6 (d), 34.2 (d), 38.5 (s), 126.9 (d), 128.2 (d), 215.3 (s); mass spectrum (70 eV), *m/e* (relative intensity) 150 (M^+, 41), 135 (6), 121 (15), 107 (32), 93 (B, 100), 79 (60), 53 (20), 39 (45); calcd for $C_{10}H_{14}O$ *m/e* 150.1045, found *m/e* 150.1049.

6β-(3,3-Dimethylcyclopent-1-enyl)-1β-methylbicyclo-[3.1.0]hexan-2-one (27). A 250-mg (0.0011 mol) sample of diazo ketone **26** and 25 mg of $Cu(acac)_2$ in 40 mL of benzene were refluxed for 12 h. Filtration of the solution through a short column of neutral alumina and evaporation gave 209 mg (96.7%) of cyclopropane **27**: bp 90–105 °C (0.1 mm, Kugelrohr); IR (neat) 1716, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 3 H), 1.07 (s, 3 H), 1.10 (s, 3 H), 1.85 (s, 1 H), 2.1 (br s, 5 H), 2.4 (d, 4 H, $J \simeq 3$ Hz), 5.4 (s, 1 H); ^{13}C NMR (C DCl_3) δ 8.7 (q), 21.8 (t), 29.9 (q, 2 methyl groups), 30.8 (d), 31.9 (t), 32.4 (d), 38.4 (s), 39.7 (s), 47.6 (t), 51.2 (t), 126.2 (d), 137.8 (s), 215.9 (s); mass spectrum (70 eV), *m/e* (relative intensity) 204 (M^+), 189 (B, 62), 147 (39), 133 (29), 106 (50), 104 (85), 96 (43), 91 (8), 77 (42); calcd for $C_{14}H_{20}O$ *m/e* 204.1514, found *m/e* 204.1520.

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 2–5 min. The eluents were condensed under vacuum (0.05–0.01 mm) in a liquid nitrogen cooled trap. Crude mixtures were then purified by medium-pressure liquid chromatography (silica gel; hexane–ether).

***cis*-Bicyclo[3.3.0]oct-6-en-2-one (14)**: at 580 °C (oven temperature on pyrolysis); yield 65%; IR (neat) 1746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.2 (m, 4 H), 2.2–2.4 (m, 3 H), 3.1 (m, 1 H), 5.4 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.3 (t), 36.3 (t), 37.4 (t), 47.7 (d), 49.3 (d), 131.1 (d), 133.8 (d), 223.7 (s); mass spectrum (70 eV), *m/e* (relative intensity) 122 (M^+, 93), 94 (92), 86 (91), 84 (87), 81 (93), 80 (87), 79 (98), 67 (94), 65 (73), 56 (92), 55 (51), 49 (74), 47 (74), 39 (61); calcd for $C_8H_{10}O$ *m/e* 122.0732, found *m/e* 122.0729.

1-Methyl-*cis*-bicyclo[3.3.0[oct-6-en-2-one (17): at 580 °C (oven temperature on pyrolysis); yield 70%; IR (neat) 1738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (s, 3 H), 1.6–2.9 (m, 6 H), 3.1 (m, 1 H), 5.5 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.6 (q), 23.9 (t), 36.2 (t), 45.0 (t), 49.3 (d), 54.6 (s), 130.7 (d), 133.8 (d), 225.3 (s); mass spectrum (70 eV), *m/e* (relative intensity) 136 (M^+, 42), 108 (73), 93 (55), 79 (B, 100), 28 (65), 18 (55); calcd for $C_9H_{12}O$ *m/e* 136.0888, found 136.0890.

2-Methyl-3-(1-prop-1-enyl)cyclopent-2-enone (19). Chromatography of the pyrolysis condensate of 350 mg of cyclopropane **16** gave (1:1 hexane–ether, silica) 81 mg (23%) of enone **19**: IR (neat) 1686, 1640, 1604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8 (s, 3 H), 1.98 (d, 3 H, *J* = 6 Hz), 2.3 (t, 2 H, *J* = 7 Hz), 2.6 (t, 2 H, *J* 7 Hz), 6.4 (br q, 1 H), 6.8 (d, 1 H, *J* = 16 Hz); ^{13}C NMR ($CDCl_3$) δ 7.9 (q), 19.1 (q), 25.7 (t), 33.6 (t), 126.6 (d), 134.2 (s), 134.9 (d), 164.1 (s), 209.8 (s).

2-Methylene-3-(*cis*-1-prop-1-enyl)cyclopentanone (18). Controlled pyrolysis of cyclopropane **16** on otherwise unconditioned Pyrex glass at 400 °C gave a 91% yield of **18**: IR (neat) 1726, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6 (d, 3 H, *J* = 6 Hz), 2.3 (m, 4 H), 3.6 (m, 1 H), 5.1 and 6.0 (dd, 1 H each, *J* = 2 Hz, exocyclic CH_2), 5.4 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.2 (q), 26.7 (t), 36.6 (t), 39.1 (d), 116.1 (t), 125.2 (d), 130.8 (d), 147.2 (s), 205.0 (s); mass spectrum (70 eV), *m/e* (relative intensity) 136 (M^+, 69), 121 (77), 108 (35), 93 (60), 80 (52), 79 (B, 100), 55 (35), 41 (40); calcd for $C_9H_{12}O$ *m/e* 136.0888, found *m/e* 136.0892.

8α-Methylbicyclo[3.3.0]oct-6-en-2-one (22a) and Its 8β Epimer (22b). Pyrolysis of **21** at 600 °C gave 18% of **22a**, 48% of **22b**, and ~20% of enone byproducts. For **22a**: IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, 3 H, *J* = 7 Hz), 2.2 (m, 4 H), 2.8 (m, 1 H), 3.1 (q, 1 H, *J* = 7 Hz), 3.4 (m, 1 H), 5.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.2 (q), 25.2 (t), 36.3 (t), 45.6 (d), 46.5 (d), 57.6 (d), 132.3 (d), 137.3 (d), 223.4 (s). For **22b**: IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (d, 3 H, *J* = 7 Hz), 2.2 (m, 4 H), 2.8 (m, 1 H), 3.1 (q, 1 H, *J* = 7 Hz), 3.4 (m, 1 H), 5.5 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.4 (q), 25.6 (t), 38.5 (t), 43.5 (d), 48.5 (d), 51.9 (d), 132.1 (d), 136.9 (d), 220.4 (s); mass spectrum (70 eV), *m/e* (relative intensity) 136 (M^+, B, 100), 121 (22), 108 (45), 93 (30), 80 (68), 79 (55), 66 (32); calcd for $C_9H_{12}O$ *m/e* 136.0888, found *m/e* 136.0886.

1α,8α-Dimethyl-*cis*-bicyclo[3.3.0]oct-6-en-2-one (25a) and Its 8β Epimer (25b). Chromatography of the crude condensate from the pyrolysis of **24** at 600 °C (1:1 hexane–ether, silica) gave 28% of **25a**, 35% of **25b**, and ~20% of enone byproducts. For **25a**: IR (neat) 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (d, 3 H, *J* = 7 Hz), 1.08 (s, 3 H), 1.4–2.2 (m, 4 H), 2.6 (m, 1 H), 3.1 (m, 1 H), 5.5 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.6 (q), 16.4 (q), 22.9 (t), 35.5 (t), 46.3 (d), 53.1 (d), 57.3 (s), 132.4 (d), 138.2 (d), 223.6 (s). For **25b**: IR (neat) 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (d, 3 H, *J* = 7 Hz), 1.09 (s, 3 H), 1.8–2.4 (m, 4 H), 2.7 (m, 1 H), 3.1 (m, 1 H), 5.6 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.0 (q), 21.6 (q), 24.1 (t), 38.7 (t), 51.6 (d), 55.9 (d), 56.9 (s), 131.7 (d), 136.4 (d), 225.9 (s); mass spectrum (70 eV), *m/e* (relative intensity) 150 (M^+, 60), 135 (18), 122 (82), 107 (38), 94 (70), 91 (60), 79 (B, 100), 55 (30), 39 (52); calcd for $C_{10}H_{14}O$ *m/e* 150.1045, found *m/e* 150.1046.

1,9,9-Trimethyl-6,7-dehydro-*cis*,*anti*,*cis*-tricyclo-[6.3.0.0^{2,6}]undecan-2-one (28a) and Its Cis,syn,cis Epimer (28b). A sample of **27** (204 mg, 0.001 mol) was evaporated at 580 °C through a Vycor tube which was previously washed with a slurry of lead carbonate in water and dried. The crude condensate (200 mg, 98%) was chromatographed to obtain 134 mg (65.5%) of **28a**, 23 mg (11.2%) of **28b**, and 30 mg of a bicyclic enone byproduct which was not further identified. Compounds **28a** and **28b** could be obtained as a mixture by filtration of the crude condensate through Celite. For **28a**: IR (neat) 1740, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (s, 3 H), 1.05 (s, 3 H), 1.07 (s, 3 H), 1.2–2.8 (m, 8 H), 3.0–3.2 (m, 2 H), 5.2 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.7 (q), 26.3 (t), 30.5 (q), 31.0 (q), 38.9 (t), 39.9 (t), 40.2 (t), 42.3 (s), 55.9 (d), 56.8 (s), 59.8 (d), 120.9 (d), 151.3 (s), 223.9 (s); mass spectrum (70 eV), *m/e* (relative intensity) 204 (M^+, 25), 189 (10), 176 (B, 100), 161 (35), 105 (32), 91 (60), 77 (30); calcd for $C_{14}H_{20}O$ *m/e* 204.1514, found *m/e* 204.1517. For **28b**: IR (neat) 1738, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 3 H), 1.04 (3 H), 1.2 (s, 3 H), 1.2–2.4 (m, 8 H), 3.0 (m, 1 H), 3.3 (m, 1 H), 5.05 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.2 (q), 23.4 (t), 30.1 (q), 30.6 (q), 38.9 (t), 39.9 (t), 41.2 (t), 42.4 (s), 56.9 (s), 50.2 (d), 61.7 (d), 120.3 (d), 153.5 (s), 223.4 (s); mass spectrum (70 eV), *m/e* (relative intensity) 204 (M^+, B, 100), 189 (40), 176 (20), 161 (35), 148 (60), 91 (75), 55 (50); calcd for $C_{14}H_{20}O$ *m/e* 204.1514, found *m/e* 204.1513.

Rhodium-Promoted Rearrangement. Typically a mixture of 0.0001 mol of the appropriate vinylcyclopropane (**13**, **16**, **21**, **24**, and **27**) and 40 mg of $(C_2H_4)_2Rh(acac)$ (0.0001 mol) in 20 mL of benzene (degassed with argon prior to use) was refluxed under argon for 48 h. In the case of **27**, toluene, xylenes, and mineral oil were also used as solvents in these reactions. The progress and the total yield were monitored by gas chromatography (Carbowax 1500). The products were isolated by washing the mixtures with 20% potassium cyanide solution followed by removal of solvents. The reaction times were considerably shortened by performing the reaction in a sealed tube. The following compounds (yields in percent) were obtained: **14** (70), **17** (75), **22a** (62), **22b** (5), **25a** (58), **25b** (6), **28a** (68), **28b** (0).

1,9,9-Trimethyl-*cis*,*anti*,*cis*-tricyclo[6.3.0.0^{2,6}]undecan-2-one (30a). A 102-mg sample of tricyclic ketone **28a** in 50 mL of hexane was hydrogenated at 50 psi of H_2 over Pd/C (5%) for 8 h. Filtration and evaporation gave 100 mg (97.1%) of **30a** as an oil, which slowly crystallized: mp 46 °C (lit.[36] mp 44–45 °C); IR (neat) cm^{-1} 1738; ^1H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 0.95 (s, 3 H), 1.03 (s, 3 H), 1.2–2.5 (m, 13 H); ^{13}C NMR ($CDCl_3$) δ 17.3 (q), 22.4 (t), 26.6 (q), 29.3 (q), 29.7 (t), 34.2 (t), 37.7 (t), 41.2 (s), 41.9 (d), 43.4 (d), 46.8 (d), 48.9 (t), 59.3 (s), 224.5 (s); mass spectrum (70 eV), *m/e* (relative intensity) 206 (M^+, 40), 191 (12), 163 (15), 110

(98), 97 (B, 100), 79 (40) 55 (40); calcd for $C_{14}H_{22}O$ *m/e* 206.1670, found *m/e* 206.1667.

1,9,9-Trimethyl-*cis*,*syn*,*cis*-tricyclo[6.3.0.0^{2,6}]undecan-2-one (30b). Hydrogenation of **28b** under the conditions described above gave a 96% yield of **30b**: IR (neat) 1739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 0.98 (s, 3 H), 1.05 (s, 3 H), 1.4–2.6 (m, 13 H); mass spectrum (70 eV), *m/e* (relative intensity) 206 (M^+, 15), 162 (15), 107 (50), 93 (60), 79 (65), 55 (80), 41 (B, 95); calcd for $C_{14}H_{22}O$ *m/e* 206.1670, found *m/e* 206.1676.

Isomerization of 28a and 28b. A mixture of **28a** and **28b** (40 mg) was refluxed for 12 h in 80% aqueous ethanol containing 5 mg of rhodium trichloride trihydrate. Filtration through alumina gave an oil [36 mg (90%); IR 1736 cm^{-1}] whose ^{1}H NMR spectrum lacked any olefinic absorption. Hydrogenation of this material over Pd/C (5%) gave 33 mg (81%) of ketone **30a**. The isomerization could also be effected in toluene (reflux, 16 h) containing *p*-toluenesulfonic acid, but lower yields were obtained at the expense of fragmentation products.

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Registry No. 1, 1001-93-0; 2, 922-65-6; 3, 50999-04-7; **4b**, 71779-51-6; **5**, 75283-35-1; **7**, 75283-36-2; **8**, 38312-94-6; **9**, 75283-37-3; **10a**, 75283-38-4; **10b**, 75283-39-5; **12**, 75283-40-8; **13**, 73522-96-0; **14**, 32405-38-2; **15**, 75283-41-9; **16**, 75283-42-0; **17**, 75283-43-1; **18**, 75299-07-9; **19**, 75283-44-2; **20**, 75283-45-3; **21**, 75283-46-4; **22a**, 75283-47-5; **22b**, 75283-48-6; **23**, 75283-49-7; **24**, 75283-50-0; **25a**, 75283-51-1; **25b**, 75331-62-3; **26**, 75283-52-2; **27**, 75283-53-3; **28a**, 75283-54-4; **28b**, 75331-63-4; **30a**, 75331-64-5; **30b**, 75331-65-6; 4,6-heptadienoyl chloride, 75283-55-5; 4,6-octadienoyl chloride, 75283-56-6; 5-(4,4-dimethylcyclopent-1-enyl)-4-pentenoyl chloride, 75283-57-7; 4,6-heptadienoic acid, 75283-35-1; 4,6-octadienoic acid, 75283-36-2; 5-(4,4-dimethylcyclopent-1-enyl)-4-pentenoic acid, 75283-39-5; dimethyl 2-(2,4-pentadien-1-yl)propanedioate, 75283-58-8; 2-(2,4-pentadien-1-yl)propanedioic acid, 75283-59-9; dimethyl 2-(2,4-hexadien-1-yl)propanedioate, 75283-60-2; 5,5-dimethyl-*cis*-2,3-epoxycyclohexanol, 38309-46-5; ethyl formate, 109-94-4; vinyl bromide, 593-60-2; triethyl orthoacetate, 78-39-7; dimethyl malonate, 108-59-8; oxalyl chloride, 79-37-8; diazomethane, 334-88-3; diazoethane, 1117-96-0; 2-chloro-7-(4,4-dimethylcyclopent-1-enyl)-6-hepten-3-one, 75283-61-3.

Stereochemistry of Addition of the Allyl Grignard Reagent to Hydroxybicyclo[2.2.1]hept-2-enes[1]

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Reactions of *syn*-bicyclo[2.2.1]hept-2-en-7-ol with an excess of allylmagnesium chloride in tetrahydrofuran or of allylmagnesium bromide in diethyl ether furnish an addition product shown to be 2-*exo*-allyl-*syn*-bicyclo[2.2.1]heptan-7-ol. Reactions of *endo*-bicyclo[2.2.1]hept-5-en-2-ol with the same reagents and with diallylmagnesium in ether furnish a compound shown to be 5-*endo*-allyl-*endo*-bicyclo[2.2.1]heptan-2-ol. A metalated hydroxyl group must play an active role in facilitating these additions since they proceed more rapidly than addition to the parent hydrocarbon, bicyclo[2.2.1]hept-2-ene, which furnishes 2-*exo*-allylbicyclo[2.2.1]heptane. They must also be considerably more rapid than additions to the epimeric alcohols (*anti*-bicyclo[2.2.1]hept-2-en-7-ol and *exo*-bicyclo[2.2.1]hept-5-en-2-ol) since no addition products were obtained from reactions with these alcohols. Attachment of the allyl group to the double bond of each bicycloheptenol from the side nearer the hydroxyl group suggests that at the time of addition the allyl is associated with the metalated hydroxyl group.

Eisch and Husk reported that allylmagnesium bromide (in excess) adds under mild conditions to the double bond of 1 (eq 1).[3] This addition was remarkable because under comparable conditions even the particularly reactive allyl Grignard reagent does not add to unstrained, nonconjugated alkenes. The hydroxyl group of 1 certainly reacts instantaneously with 1 mol of the Grignard reagent. The metalated hydroxyl group that results must in some manner facilitate the ready addition to the double bond.

$$\underset{\mathbf{1}}{CH_2{=}CHCH_2C(OH)Ph_2} \xrightarrow[2.\ H_2O]{1.\ CH_2{=}CHCH_2MgBr} CH_2{=}CHCH_2CH_2CH_2CH_2C(OH)Ph_2 \quad (1)$$

A variety of additions of Grignard reagents to alkenols[4-8] have since been reported, as have similar additions to alkynols[6,9-11] and allenols.[12] Other functional groups, particularly amino and alkoxyl, have also been found to exert a promoting effect on Grignard reagent additions to carbon–carbon multiple bonds.[5,11,13] Hydroxyl and other

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