Tetrahedron Vol. 37, No. 25, pp. 4401 to 4410, 1981
Printed in Great Britain.

0040-4020/81/254401-10$02.00/0
Pergamon Press Ltd.

BICYCLOPENTANOID SESQUITERPENES. THE SYNTHESIS OF CEDRANOID SESQUITERPENES VIA THE PHOTO-REARRANGEMENT OF BICYCLO[2.2.2]OCTENONES[1]

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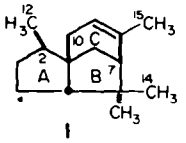
(*Received in U.S.A.* 9 *February* 1981)

Abstract—(±) - *exo* - 2,6,6 - Trimethyltricyclo[5.3.1.0^{1,5}]undecane - 8,10 - dione (**11**) has been synthesized from dimethyl 6,6 - dimethyl - 5 - oxobicyclo[2.2.2]oct - 7 - ene dicarboxylate (**17**). This constitutes a new synthesis of cedrol (**3**) since **11** has previously been converted to this compound.

Two groups of sesquiterpenes incorporate two fused 5-membered rings; both have tricyclo[5.3.1.0^{1,5}]undecane skeletons. They differ in the positioning of the four additional carbon atoms as exemplified by α-cedrene (**1**)[2,3] and α-patchoulene (**2**).[4] Our concern here is with the first group, the cedranoid sesquiterpenes. This includes in addition to **1** and the closely related cedrol, **3**, a variety of more highly oxygenated compounds, such as shellolic acid (**4**),[5] laccishellolic acid (**5**),[6] and α-pipitzol (**6**).[7] The first total synthesis of a cedranoid sesquiterpene was achieved by Stork and Clarke[8] who synthesized cedrol (**3**) by a route involving formation of the bicyclo[3.3.0]octane ring A/B system (**7**) via an aldol condensation and subsequent closure of ring C. Their synthesis of **3** was followed by several total syntheses of **1** and **3** inspired by biogenetic considerations[9] that involved formation of the spiro[4.5]decane ring A/C system (**8**) followed by closure of ring B[10] or a related sequence.[11] In a different approach Breitholle and Fallis[12] have recently synthesized **3** via ring expansion of a compound with a tricyclo[5.2.1.0^{1,5}]decane system (**9**). The only more highly oxygenated cedranoids that have been synthesized are α-pipitzol (**6**) and its β isomer which were formed by thermal isomerization of perezone (**10**).[7]



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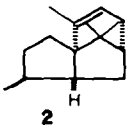

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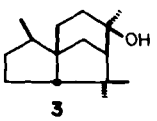

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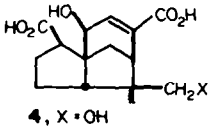
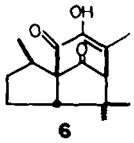


4, X = OH
5, X = H



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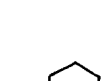
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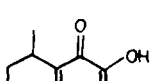

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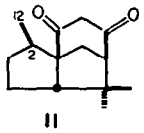
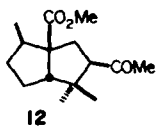
Many of these routes appears to be readily applicable to the synthesis of many of the more highly oxygenated cedranoids and we embarked on a new synthetic approach to cedrol (**3**) that was designed to be applicable to the eventual incorporation of oxygenated functions at C-10, C-12, C-14, and C-15. We chose as our target the β-diketone **11**, a pivotal intermediate in the synthesis of Stork and Clarke,[8] which they obtained by base-catalyzed cyclization of the keto ester **12**. This intermediate clearly has the potential of serving as a source of cedranoids with oxygenated functions at C-10 and C-15. We describe now a synthesis of **11** that is potentially adaptable to the introduction of oxygenated functions at C-12 and C-14 also.



11



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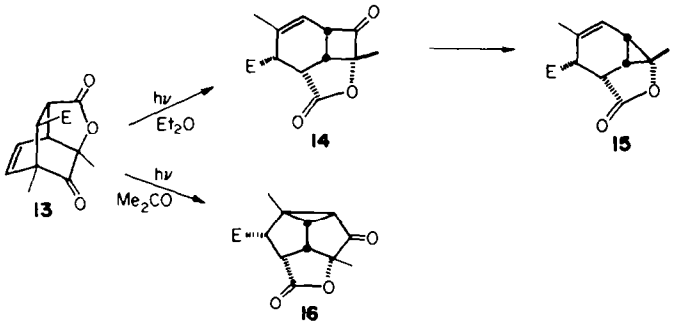
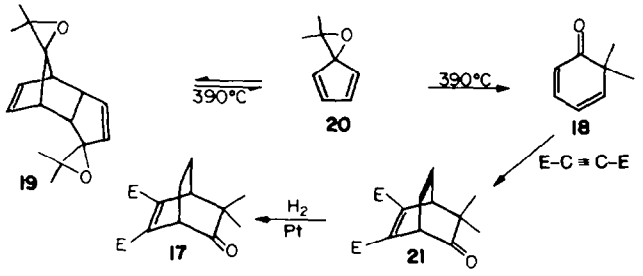
Our synthetic strategy had its origin in observations that we had made during an investigation of the photochemistry of bicyclo[2.2.2]octenones formed by modified Wessely oxidation of *ortho*-substituted phenols.[13] Ketone **13**, obtained by oxidation of 2,6-dimethylphenol with lead tetraacetate in the presence of excess methyl hydrogen maleate, gave on direct irradiation in ether the cyclobutanone **14** and its decarbonylation product **15**,[14] while on sensitized photolysis in acetone it gave the tricyclo[3.2.1.0^{2,8}]octan-3-one derivative **16** (Scheme 1). Formation of **14** involves a 1,3-acyl migration and that of **16** a 1,2-acyl migration (oxa-di-π-methane rearrangement); such reactions are well known for related compounds[15] and other types of β,γ-unsaturated ketones.[16] This investigation led us to consider the utilization of the photosensitized oxa-di-π-methane rearrangement of a suitably substituted bicyclo[2.2.2]octenone for the synthesis of the bicyclo[3.3.0]octane system of the cedranoid sesquiterpenes.[17] We envisaged that homoconjugate addition to the cyclopropane ring of the tricyclo[3.2.1.0^{2,8}]octan-3-one[18] would provide a route for the stereoselective introduction both of the C-12 methyl



Scheme 1. (E = CO_2Me).



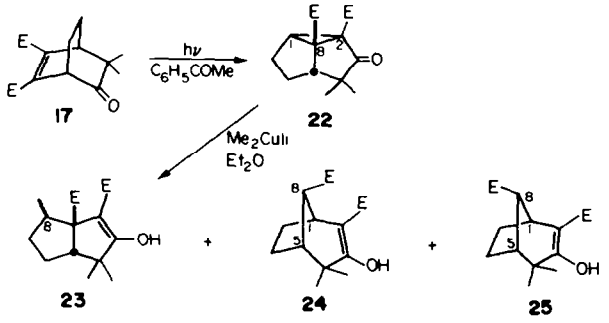
Scheme 2. (E = CO_2Me).

group at C-2 in **11** and of other groups that could be converted to the functionalized substituents at this carbon in the more highly oxygenated cedranoids.

We choose **17** as our starting bicyclo[2.2.2]octenone, which we had prepared by the route shown in Scheme 2 in the course of another investigation.[19] 6,6-Dimethyl-2,4-cyclohexadienone (**18**), obtained by thermolysis of **19**, a dimer of 6,6-dimethylfulvene 5,6-epoxide (**20**),[20] gave the adduct **21** with dimethyl acetylenedicarboxylate in boiling xylene, which on hydrogenation over platinum underwent reduction of the unconjugated ethylenic double bond only to give **17**.

Photolysis of **17** with acetophenone as both sensitizer and solvent gave the desired oxa-di-π-methane rearrangement product **22** in 76% yield (Scheme 3). This showed bands at 5.75 and 5.79 μ in its IR spectrum and no vinyl proton signals in its ^1H NMR spectrum excluding the possibility that it was a 1,3-acyl migration product of type **14**. Interestingly, photolysis of **13** was sensitized by acetone ($E_T \sim 80$ kcal/mol[21]) but not by acetophenone ($E_T \sim 74$ kcal/mol[21]). Observations on β,γ-unsaturated ketones suggest that they have triplet energies in the range 74–80 kcal/mol.[22] The present results indicate that the triplet energies of **13** and **17** fall in this range with that of the latter being lower than that of the former; this relationship may be attributed to skeletal distortion in the former[13] and/or the presence of the carbomethoxy substituents in the latter.

Reaction of **22** with lithium dimethylcuprate in ether gave the desired product **23** in 75% yield together with

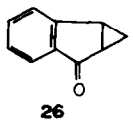


Scheme 3. (E = CO_2Me).

two minor products **24** and **25** (Scheme 3); one of the minor products was very difficult to separate from **23** and complete purification of the latter was attended by considerable losses. However, ^{1}H NMR spectroscopic analysis of the crude reaction product showed that the ratio of major to combined minor products was 14 : 1. The gross structure of **23** was readily assigned on the basis of spectroscopic data. Its IR spectrum showed strong bands at 6.08 and 6.20 μ, and a broad shallow band at 3.0–3.5 μ, consistent with the presence of an enolized β-keto ester group, together with a strong band at 5.82 μ, in accord with the presence of an ester group on a quaternary carbon atom. Its ^{1}H NMR spectrum included signals at δ 1.11 (s, 6H) and 1.13 ppm (d, J = 6 Hz, 3H), attributable to the *gem*-dimethyl groups and the methyl group at C-8, respectively, and a one-proton singlet at δ 10.85 as expected for an enolic proton.

The relative configuration at C-8 was assigned in the expectation that addition of the methyl group to **22** would occur with inversion of configuration in analogy with related homoconjugate addition reactions of lithium cuprate reagents.[18,23] This assignment was eventually verified by the successful outcome of the synthesis of **11**. The ^{13}C NMR spectrum of **23** showed three C-methyl signals at δ 16.1, 19.4 and 28.0 ppm; comparison of these values with the chemical shifts of the C-methyl groups of analogous compounds indicated that the C-8 methyl group gives rise to the signal at δ 16.1 ppm. This high field position is more characteristic of an *endo* C-8 methyl group in simple bicyclo[3.3.0]octanes,[24] but in **23** the C-1 methyl ester group is expected to exert a large γ shielding effect on the *exo* C-8 methyl group.

As in related cases[18,23] the cyclopropyl bond of **22** that undergoes cleavage to give **23** is the one best oriented to give rise to maximum overlap of the developing carbanion with both the ketone and the C-2 ester carbonyl groups. It is of interest that when the treatment of **22** with lithium dimethylcuprate was attempted in tetrahydrofuran very little reaction occurred. The use of this solvent was suggested by earlier work in which it had been found that the reaction of **26** with lithium dimethylcuprate gave inproved yields of the homoconjugate addition product **27** when the solvent was changed from ether/pentane to ether/tetrahydrofuran or ether/dimethoxyethane.[25] This type of effect has been interpreted in terms of increased nucleophilicity of the orgamometallic cluster resulting from improved coordination of the solvent with lithium ions.[26,27] In the present case it may be suggested that reaction of **22** with lithium dimethylcuprate requires prior coordination with a lithium ion to give **28**, such coordination both increasing electron withdrawal from the cyclopropane ring and maintaining an optimal orientation of the ketone and C-2 ester carbonyl groups for delocalization of the developing anion. In tetrahydrofuran improved solvation of the lithium ions could retard or inhibit the formation of **28**. This observation finds analogy in the retardation of the reactions of oxiranes with lithium dimethylcuprate in tetrahydrofuran relative to ether solution.[28] The postulated intermediacy of **28** in the reactions of **22** with lithium dimethylcuprate may also account for the observation that two equivalents of the latter reagent were required for the reaction to proceed at a practicable rate.[29]



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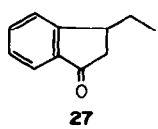

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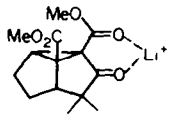
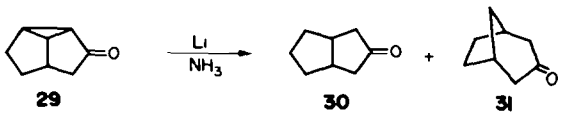


28

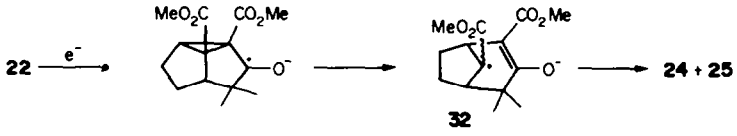
We return now to the assignment of the structures of the minor products **24** and **25** from the reaction of **22** with lithium dimethylcuprate. One of these, **25**, was observed mixed with **23** in small amounts on chromatography of the crude reaction mixture, its presence being vouchsafed by peaks at δ 1.20, 1.29, and 12.11 ppm in the ^{1}H NMR spectra of the chromatographic fractions. The other minor product, **24**, could be cleanly separated from **23** by chromatography; its IR spectrum resembled that of **23** and its ^{1}H NMR spectrum included two three-proton singlets at δ 1.13 and 1.19 ppm, two one-proton multiplets at δ 2.40 and 3.24 ppm, a one-proton triplet (J = 4 Hz) at δ 2.67 ppm, and a one-proton singlet at δ 12.15 ppm. The mass spectrum of **24** exhibited a peak at *m/e* 268, indicating that it was a reduction product of **22** and suggesting that it arose by reduction of the cyclopropane ring, as did its IR and ^{1}H NMR spectra which indicated the presence of an enolized β-keto ester grouping.

Since insufficient material was available for full characterization of these minor products, we undertook a study of the reduction of **22** with lithium in liquid ammonia. This gave a ~1 : 1 mixture of two products whose spectra were identical to those of the minor products from the reaction of **22** with lithium dimethylcuprate; these were separated and individually characterized. Their IR and ^{1}H NMR spectra confirmed that both incorporate an enolized β-keto ester grouping, and the multiplicities of the signals in their SFORD ^{13}C NMR spectra showed that they both arise by reductive cleavage of the C-2–C-8 bond of **22** to give a bicyclo[3.2.1]octane system rather than by cleavage of the C-1–C-2 bond to give a bicyclo[3.3.0]octane system. It was concluded that these products are epimers at the C-8 position of compounds with gross structures corresponding to **24** and **25**. The individual structural assignments were made on the basis of an analysis of their ^{1}H NMR spectra (Table 1). Inspection of a molecular model of **24** shows that the dihedral angle between the (C-1)-H and (C-8)-H bonds is ~45°, as is that between the (C-5)-H and (C-8)-H bonds; this would result in the splitting of the C-8 proton signal into a triplet with J ~ 4 Hz.[30] Thus the reduction product whose spectrum included a one-proton triplet (J = 4 Hz) at δ 2.67 ppm was assigned this structure. On the other hand, a model of **25** indicated that the corresponding dihedral angles are ~90°, which would be expected to result in negligible coupling between the C-8 proton signal and the C-1 and C-5 protons. Accordingly, the signal at δ 2.86 ppm assigned to the C-8 proton in the spectrum of the other reduction product is a singlet, and this product is assigned structure **25**. That **24** and **25** are epimers was confirmed by the conversion of **24** to a mixture of **24** and **25** on treatment with methanolic sodium methoxide.

It has previously been reported that reduction of the parent tricyclo[3.2.1.0^{2,8}]octan-3-one (**29**) with lithium in liquid ammonia gives bicyclo[3.3.0]octan-3-one (**30**) as



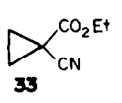
Scheme 4.



Scheme 5.

the major product (95%) and only a minor amount (5%) of bicyclo[3.2.1]octan-3-one (**31**) (Scheme 4).[31] This was interpreted in terms of preferential cleavage of the cyclopropyl bond that has greater overlap with the π-orbital of the ketonic group.[32] That reduction of **22** gives only bicyclo[3.2.1]octane derivatives, contrary to the case of **29**, is accountable to the presence of the C-8 ester group; this must favor C-2–C-8 bond cleavage because of stabilization of the anion radical **32** (Scheme 5).

The formation of **24** and **25** in the reaction of **22** with lithium dimethylcuprate was an unexpected, but interesting, nuisance. To our knowledge there is no previous report of the reduction of an activated cyclopropane with a lithium organocuprate reagent. Reduction of α,β-unsaturated ketones[26,33] and oxiranes[28] in reactions with the thermally unstable cuprates prepared from *s*- and *t*-butyllithium have been attributed to unidentified copper hydride species formed by decomposition of the cuprates, probably involving transfer of a β-hydrogen to the copper atom and elimination of an alkene.[26,34] However, there is no evidence that lithium dimethylcuprate in ether solution is unstable under the conditions (0°) of its reaction with **22**, and indeed its stability has been attributed to the absence of β-hydrogen atoms.[33] Furthermore, lowering the reaction temperature to −15° did not change the amounts of **24** and **25** formed. A more likely interpretation of the formation of these products can be advanced on the basis of the extensive investigation of the reactions of α,β-unsaturated carbonyl compounds with lithium organocuprates, which has established that these reactions proceed via electron transfer.[26,35,36] α,β-Unsaturated carbonyl compounds whose reduction potentials are more negative than −2.35 V do not undergo conjugate addition with lithium dimethylcuprate,[35] and they either do not react or undergo enolization or slow 1,2-addition to the carbonyl group.[37] Activated cyclopropanes that undergo homoconjugate addition with lithium organocuprates, such as **33** and **34**, have reduction potentials that are too low to permit reaction via an initial electron transfer (E_{red} −2.93



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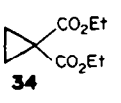
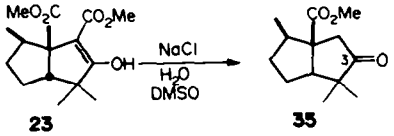


34

and −2.98 V, respectively),[38] and House[35] has proposed that in the case of such cyclopropane derivatives, unlike those of α,β-unsaturated carbonyl compounds, homoconjugate addition occurs by nucleophilic displacement rather than by initial electron addition. In the present case, although the reduction potential of **22** is not known, it may be anticipated that the ketonic group and C-8 ester group will increase this potential relative to **34**,[39] and raise it close enough to −2.35 V to permit a small amount of electron transfer from lithium dimethylcuprate. The resulting anion radical, **32**, must then undergo further reduction competitively with rebonding or methyl transfer.

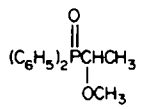
Revenons à nos moutons. We now discuss the elaboration of compound **23** to the β-diketone **11** by the construction of ring C. The carbomethoxy group at C-2, having served its purpose in activating and directing homoconjugative addition to the cyclopropane ring of **22**, was first removed. Decarbomethoxylation was effected by the Krapcho procedure, involving treatment with sodium chloride in hot, aqueous dimethyl sulfoxide.[40] This gave the keto ester **35** in 74% yield (Scheme 6), whose ^{1}H NMR spectrum clearly showed the C-2 methylene proton signals as an AB doublet of doublets with J = 20 Hz, as expected for the geminal coupling of protons adjacent to a carbonyl group.[41]

Our next aim was to add a two-carbon chain at C-3 in **35** that would permit the closure of ring C. Our initial attempts sought to use Wittig-type reactions for this purpose. Pursuing a contemporaneous preliminary report,[42] we investigated the applicability of the lithio derivative of **36**, whose addition to aldehydes was described. Model studies with benzophenone did on one occasion give a ~20% yield of 1,1-diphenylacetone but on others returned only starting materials. Reactions with **35** were not successful even to this meager extent, uniformly returning starting materials. When the reaction was attempted in tetrahydrofuran at −75° addition of **35** to the deep red solution of the anion of **36** immediately discharged the color, and we therefore conclude that enolate ion formation preempts addition.[43,44] When the reaction was attempted at −95°[44] the color of the anion persisted for several hours; subsequent warming of the reaction mixture to −80° led to rapid disappearance of the color,



23 **35**

Scheme 6.



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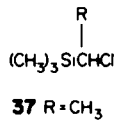
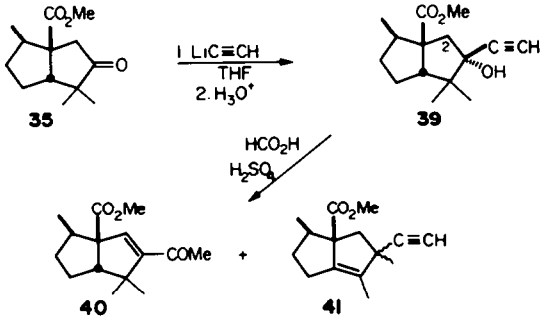


37 R = CH_3

38 R = H

but workup again gave only starting materials.[45] We were equally unsuccessful in inducing the lithio derivatives of the α-chloroalkylsilanes **37**[46] and **38**[47] to react with **35**; here the difficulties were probably due to steric hindrance, since lithiated **38** adds readily to cyclopentanone but gives only poor yields with camphor.[47]

With a view to minimizing steric difficulties we turned to a more classical approach to the introduction of a functionalized two-carbon substituent, *viz* reaction with lithium acetylide at −78° in tetrahydrofuran. Here success finally attended our efforts and we obtained a 61% yield of the desired propargylic alcohol **39** (Scheme 7); the ^{1}H NMR spectrum of the crude reaction product showed that ~30% of **35** was unconsumed, presumably as a result of competitive enolate ion formation, since attempts to force complete conversion of **35** to **39** by use of the lithium acetylide-ethylenediamine complex[48] or by using a mixture of pentane and tetrahydrofuran as solvent[48b] were unsuccessful. The presence of hydroxyl and terminal acetylenic groups in the product was evidenced by its IR spectrum, which showed peaks at 2.79 (m, O–H stretch) and 3.03 μ (m, ≡C–H stretch), although the C≡C stretching band was too weak to be identified unambiguously. Its ^{1}H NMR spectrum, like that of **35**, showed the C-2 methylene proton signals as an AB system, but the geminal coupling constant is reduced from 20 to 14 Hz in the absence of the adjacent ketonic group. Its SFORD ^{13}C NMR spectrum includes doublets at δ 73.0 and 85.3 ppm that are assigned to the terminal and non-terminal acetylenic carbons, respectively; the residual coupling shown by the former signal is 72 Hz, attributable to the very large ^{1}J C–H coupling constant for acetylenic carbon (~250 Hz), and that shown by the latter signal is 14 Hz, attributable to the unusually large ^{2}J C–H coupling constant for the non-terminal carbon in the C≡CH group (~50 Hz).[49] The acetylenic group in **39** is assigned the *exo* configuration in the expectation that attack of the acetylide ion occurs on the less hindered side of **35**.



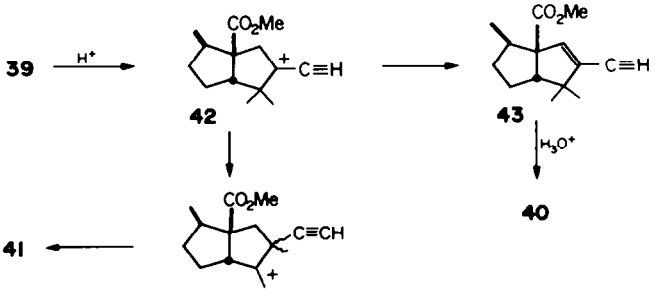
35 39 40 41

Scheme 7.

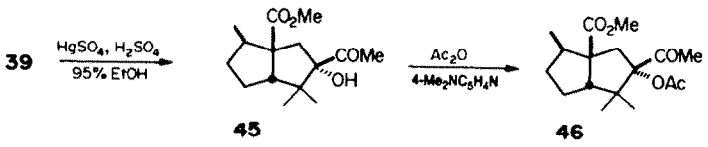
Having successfully introduced a two-carbon substituent at C-3, we now sought to convert this to an acetyl group for the construction of ring C of **11**, and to remove the extraneous hydroxyl group at C-3. To this end **39** was treated with hot 92% formic acid containing a small amount of concentrated sulfuric acid in order to convert it to **40** by a Rupe rearrangement (Scheme 7).[50] This gave a mixture of two products in a ~1.2 : 1 ratio. The elemental composition and spectra of the former product, $C_{15}H_{22}O_3$, showed it to be **40**. Its IR spectrum showed bands at 6.00 (s), 6.20 (w), and 7.37 μ (m) in accord with the presence of an α,β-unsaturated methyl ketone grouping. Its ^{1}H NMR spectrum includes signals at δ 2.29 (s, 3H) and 6.56 (s, 1H) as expected for the methyl group of a methyl ketone and the β proton of an α,β-unsaturated ketone, respectively. Its ^{13}C NMR spectrum showed a signal at δ 197.3 ppm, confirming the presence of an α,β-unsaturated ketonic group, together with signals at δ 144.0 and 149.2 ppm, attributable to the ethylenic carbons of this group.

The minor product from the treatment of **39** with formic and sulfuric acids is assigned structure **41** (Scheme 7) on the basis of its elemental composition, $C_{15}H_{20}O_2$, and spectra. Its IR spectrum, with bands at 3.13 (m) and 4.78 (vw) μ, showed that it retained the terminal acetylenic group. Its ^{1}H NMR spectrum includes signals at δ 1.75 (d, J = 1.5 Hz, 3H) and 2.27 (s, 1H), attributable to a vinyl methyl group and an acetylenic proton, respectively. The formation of **41** can readily be interpreted in terms of the postulated mechanism for the Rupe rearrangement (Scheme 8).[50] The cationic intermediate **42** can either lose a proton to give **43**, which on acid-catalyzed hydration gives **40**, or can undergo a 1,2 migration of a methyl group to give **44**, which on loss of a proton gives **41**. It was subsequently found that with anhydrous formic acid and increased concentrations of sulfuric acid the formation of **41** could be suppressed, but this was at the expense of increased polymerization and the yield of **40** remained low.

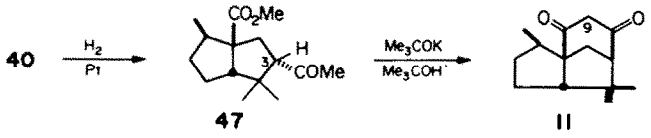
Because of this low yield we investigated an alternative reaction sequence in which **39** was converted to the α-ketol **45** and the corresponding acetate **46** (Scheme 9). However, it was not found possible to bring about reductive cleavage of either the hydroxyl or acetoxyl group under a variety of conditions.



Scheme 8.



Scheme 9.



Scheme 10.

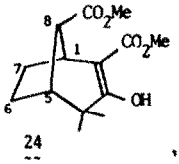
The synthesis was therefore continued via **40**. Hydrogenation of this over platinum gave a dihydro compound whose IR and ^{1}H NMR spectra [λ_{max} 5.83 μ (br); δ 2.14 (s, 3H), no vinyl proton signal] showed that it had a gross structure corresponding to **47** (Scheme 10). The acetyl group in **47** is assigned the *endo* configuration in the expectation that delivery of hydrogen occurs from the less hindered side of **40**, and **47** is thus considered to be the C-3 epimer of **12**, the intermediate that Stork and Clarke[8] cyclized to give **11**. We anticipated that **47** would also cyclize to **11** via epimerization at C-3 under the strongly basic reaction conditions and were happy to find this indeed was the case. Treatment with potassium t-butoxide in t-butyl alcohol gave (±)-**11** in good yield with solution IR ^{1}H NMR, and ^{13}C NMR spectra identical with those of a sample of optically active **11** obtained previously.[8,52] The IR spectrum ($CHCl_3$) shows a strong band at 5.88 μ with a shoulder at 5.81 μ, typical of unenolized 1,3-cyclohexanediones;[53] the ^{1}H NMR spectrum, with a two-proton singlet attributable to the protons at C-9, also shows that **11** is not significantly enolized in chloroform solution. The PND ^{13}C NMR spectrum of **11** was recorded in NaOH/D_2O and showed thirteen sharp lines and a broadened signal at $\delta \sim$ 105 ppm. The latter is assigned to C-9 in the sodium enolate of **11**; it finds its counterpart in a broadened signal at δ 103.9 ppm in the spectrum of 1,3-cyclohexanedione in NaOH/D_2O.

The synthesis of **11** from **17** completes the formal synthesis of cedrol and paves the way for an assault on the more highly oxygenated cedranoids. Our preliminary results[1] on the introduction of functionalized substituents at C-1 in **22** suggest that this approach is not without promise.

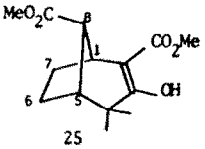
EXPERIMENTAL

M.ps were determined on a Fisher-Johns apparatus and are uncorrected. IR spectra were taken in $CHCl_3$ solution and the ^{1}H and ^{13}C NMR spectra in $CDCl_3$ solution. Analytical thin layer chromatography was carried out on 0.25 mm silica gel Q6-F plates from Quantum Industries. Preparative thin layer chromatography was carried out on 20 × 20 cm plates coated with 0.5 mm, 1 mm or 2 mm silica gel layers (Merck Kieselgel 60 PF_{254} containing gypsum). Medium pressure liquid chromatography was carried out on a Merck Silica gel 60 pre-packed column (Size B) operated at a pressure of ~5 psi. Unless otherwise stated, solutions were dried over magnesium sulfate and concentrated on a Büchi Rotovapor R rotary evaporator under water aspirator pressure. Solvents used for workups and chromatography were either distilled or were ACS Reagent grade quality. Unless otherwise stated, photolyses were carried out in a Rayonet Srinivasan–Griffin Photochemical Reactor equipped with eleven low pressure RPR lamps. Photoysis solutions were

Table 1. ^{1}H NMR spectra of **24** and **25**[a]



24



25

H	H_6CDCl_3	
1	3.24 (m)	3.30 (m)
5	2.40 (m)	2.33 (m)
6,7	1.4-2.1 (m)	1.6-2.1 (m)
8	2.67 (t, J = 4 Hz)	2.86 (s)
CCH_3	1.13 (s), 1.19 (s)	1.20 (s), 1.29 (s)
OCH_3	3.64 (s), 3.81 (s)	3.71 (s), 3.78 (s)
OH	12.15 (s)	12.11 (s)

[a]The relative intensities of the signals were in accord with the assignments.

flushed with a stream of dry nitrogen for 0.5–3 hr prior to irradiation. Solvents for photolysis were distilled prior to use.

Direct photolysis of **13**: *formation of* **14** *and* **15**.- (a) Compound **13**[13] (59 mg, 0.24 mmol) was dissolved with stirring in ether (25 ml) in a Pyrex tube. The solution was degassed with nitrogen for 2 hr, and was then irradiated at 300 nm for 3.5 hr to give a mixture of **14** and **15**. The solution was cooled to 0°, when **14** crystallized. Two recrystallizations by solution of the crystals in large volumes of ether, reduction of the volume without heating and cooling gave **14** (17 mg, 0.068 mmol, 28%), m.p. 148–153°; λ_{max} 5.60, 5.72 μ; ^{1}H NMR: δ 1.57 (s, 3H), 2.00 (m, 3H), 3.19 (t, J = 10 Hz, 1H), 3.36–4.12 (m, 2H), 3.76 (d, J = 5 Hz, 1H), 3.77 (s, 3H), 5.58 (m, 1H); ^{13}C NMR: δ 16.4 (q), 22.8 (q), 34.6 (d), 40.1 (d), 42.3 (d), 52.1 (q), 55.8 (d), 96.9 (s), 117.2 (d), 133.4 (s), 170.7 (s), 174.7 (s), 201.6 (s); *m/e* 251 (M + 1, 12%). Calc. for $C_{13}H_{14}O_5$: C, 62.39: H, 5.64; found: C, 62.53; H, 5.67%.

(b) Continued irradiation of a mixture of **14** and **15** as described above for irradiation of **13** (170 mg, 0.68 mmol) in tert-butyl alcohol (21 ml) with a Hanovia 450W medium-pressure mercury arc lamp led to the exclusive formation of **15** (111 mg, 0.50 mmol, 74%). Crystallization from ethyl acetate/pentanes (1 : 1 v/v) gave **15**, m.p. 76–78°; λ_{max} 5.64, 5.73 μ; ^{1}H NMR: δ 1.14–2.33 (m, 2H), 1.68 (s, 3H), 1.98 (m, 3H), 3.40–3.83 (m, 2H), 3.79 (s, 3H), 5.61 (m, 1H); ^{13}C NMR: δ 18.5 (q), 20.3 (q), 22.2 (d), 24.2 (d), 43.2 (d), 44.4 (d), 51.9 (q), 68.1 (s), 118.7 (d), 134.9 (s), 170.7 (s), 176.3 (s); *m/e* 223 (M + 1, 12%). Calc. for $C_{12}H_{14}O_4$: C, 64.85: H, 6.35; found: C, 64.87: H, 6.31%.

Sensitized photolysis of **13**: *formation of* **16**. A solution of **13** (800 mg, 3.2 mmol) in acetone (100 ml) in a quartz tube was degassed for 1 hr. The solution was then irradiated at 254 nm for 9.5 hr. The solvent was removed and the oily residue was crystallized from a mixture of cyclohexane (15 ml) and ethyl acetate (25 ml) to give **16** (395 mg, 1.58 mmol, 49%) as hard, white crystals. Further recrystallization gave **16**, m.p. 150.5–152°; λ_{max} 5.62, 5.74 μ; ^{1}H NMR: δ (100 Mz) 1.36 (s, 3H), 1.50 (s, 3H), 1.96 (dd, J = 5 Hz, J = 0.5 Hz, 1H), 2.64 (t, J = 5 Hz, 1H), 3.37 (dd, J = 5 Hz, J = 0.5 Hz, 1H), 3.67 (s, 3H), ~3.67 (d, J ~ 4.5 Hz, 1H; visible in $CDCl_3/C_6H_6$), 3.71 (d, J = 1 Hz, 1H); ^{13}C NMR: δ 20.5 (q), 21.1 (q), 35.8 (d), 42.1 (d), 47.4 (s), 52.3 (d, q), 53.3 (d), 55.7 (d), 89.4 (s), 171.0 (s), 174.7 (s), 206.6 (s); *m/e* 250 (21%). Calc. for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64; found: C, 62.29; H, 5.68%.

6,6-*Dimethylcyclohexa*-2,4-*dienone* (**18**). Compound **19**[20] (30.0 g, 0.123 mol) was distilled at reduced pressure (60 mm) through a hot (380°) Pyrex tube (length 25 cm, inner diameter 1.5 cm) packed with glass beads (diameter 3 mm). The product **18** (25.4 g, 0.21 mol; 85%) was collected in an ice-cooled flask as a mobile light brown liquid; ^{1}H NMR: δ 1.23 (s, 6H), 6.0–6.5 (m, 3H), 6.95–7.25 (m, 1H). The ^{1}H NMR spectrum of this material showed it to be virtually free from the by-products found by Alder, Flock and Lessenich.[20] Distillation of the crude material was avoided as it led to lower yields due to thermally induced dimerization. Dimerization also occurred on standing at room temperature, and therefore this material was used immediately.

5,6 - *Dicarbomethoxy* - 3,3 - *dimethylbicyclo*[2.2.2]*octa* - 5,7 - *dienone* (**21**). A solution of freshly prepared **18** (4.9 g, 0.040 mol) and dimethyl acetylenedicarboxylate (6.1 g, 0.043 mol) in xylene (50 ml) was boiled under reflux for 24 hr. The xylene was removed and the unconsumed dimethyl acetylenedicarboxylate was distilled under vacuum to leave crude **21** (9.46 g, 0.036 mol, 89%) as a brown oil. Alder, Flock and Lessenich[20] reported that distillation of the crude product gives **21** as a colorless oil, b.p. 118° (0.01 mm). However, in our hands distillation through a Vigreux column at 0.03 mm (b.p. 122°) did not remove all the colored impurities. The crude adduct was used without further purification; λ_{max} 5.83, 6.08 (m), 6.25 μ (w); ^{1}H NMR: δ 1.13 (s, 6H), 3.78 (s, 3H), 3.81 (s, 3H), 3.95 (dd, J = 5 Hz, J = 2 Hz, 1H), 4.46 (dd, J = 5 Hz, J = 2 Hz, 1H), 6.30–6.75 (m, 2H); ^{13}C NMR: δ 26.9 (q), 28.3 (q), 39.6 (s), 51.9 (d), 52.5 (q), 57.9 (d), 128.3 (d), 135.7 (s), 136.5 (d), 143.8 (s), 164.7 (s), 166.1 (s), 206.0 (s).

5,6 - *Dicarbomethoxy* - 3,3 - *dimethylbicyclo*[2.2.2]*oct* - 5 - *en* - 2 - *one* (**17**). Crude **21** (13.0 g, 0.049 mol) was hydrogenated at atmospheric pressure in methanol (75 ml) over platinum (*ca.* 100 mg); hydrogen uptake was complete in 24 hr. The catalyst was filtered and the filtrate was concentrated to give **17**. Two recrystallizations, one from a mixture of pentane and ethyl acetate and a second from methanol gave **17** (11.2 g, 0.042 mol, 85%) as white crystals, m.p. 59–60°; λ_{max} 5.80, 6.08 μ (w); ^{1}H NMR: δ 1.08 (s, 3H), 1.13 (s, 3H), 1.4–2.4 (m, 4H), 3.00 (m, 1H), 3.56 (m, 1H), 3.75 (s, 3H), 3.79 (s, 3H); ^{13}C NMR: δ 20.7 (t), 22.3 (t), 23.8 (q), 26.4 (q), 42.9 (s), 46.1 (d), 49.5 (d), 52.4 (q), 132.1 (s), 145.7 (s), 164.7 (s), 166.6 (s), 213.5 (s); *m/e* 266 (10%). Calc. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81; found: C, 63.08; H, 6.88%.

2,8 - *Dicarbomethoxy* - 4,4 - *dimethyltricyclo*[3.2.1.0^{2,8}]*octan* - 3 - *one* (**22**). A solution of **17** (5.0 g, 18.8 mmol) in acetophenone (225 ml) was irradiated at 350 nm for 17 hr. The acetophenone was removed by distillation at 15 mm. Crystallization of the residue from methanol gave **22** (3.8 g, 14.4 mmol, 76%). Further recrystallization from methanol gave **22** as hard white crystals, m.p. 82–83°; λ_{max} 5.75, 5.79 μ; ^{1}H NMR: δ 0.93 (s, 3H), 1.22 (s, 3H), 1.5–2.5 (m, 4H), 2.85–3.30 (m, 2H), 3.70 (s, 3H), 3.72 (s, 3H); ^{13}C NMR: δ 17.1 (q), 25.2 (q), 26.8 (q), 34.6 (t), 41.6 (d), 51.4 (d), 52.4 (q), 52.7 (s), 52.8 (q), 54.1 (s), 55.4 (s), 165.7 (s), 169.9 (s), 210.5 (s); *m/e* 267 (M + 1, 7%), 266 (3%). Calc. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81; found: C, 63.17; H, 6.89%.

1,2 - *Dicarbomethoxy* - 4,4 - exo - 8 - *trimethyl* - cis - *bicyclo*[3.3.0]*oct* - 2 - *en* - 3 - *ol* (**23**).[54] A solution of methyllithium–lithium bromide complex in ether (1.67 M; 54 ml, 90 mmol) was added over ~1 hr to a cold (0–5°), stirred slurry of cuprous iodide (8.65 g, 45 mmol) in ether (80 ml) under argon. After a further 2 hr a solution of 22 (6.00 g, 22.5 mmol) in ether (70 ml) was added over a period of ~1 hr. The reaction mixture was stirred at 0° for 12 hr and was then siphoned into cold 10% hydrochloric acid (200 ml). The resulting mixture was filtered through Celite. The filtrate was separated and the aqueous phase was extracted with ether (4 × 25 ml). The organic phases were combined and washed with saturated aq. sodium bicarbonate (25 ml). 1M aq sodium thiosulfate (25 ml), and saturated aq sodium chloride (25 ml). The ethereal solution was dried and concentrated to give a yellow oil (5.6 g) containing **23**, **24**, and **25**. The ^{1}H NMR spectrum of this oil indicated that the ratio of **23** to **24** and **25** combined was 14 : 1. Repeated crystallization of this oil from pentane containing 10% ethyl acetate gave **23** as a yellow solid (1.60 g) which was sublimed (70°, 0.03 mm) to give **23** as a white solid. Further recrystallization from pentane and sublimation gave pure **23**, m.p. 76.5–78.5°; λ_{max} 5.82, 6.08, 6.20 μ; ^{1}H NMR: δ 1.11 (s, 6H), 1.13 (d, J = 6 Hz, 3H), 1.3–2.3 (m, 5H), 2.5–2.9 (m, 1H), 3.68 (s, 3H), 3.81 (s, 3H), 10.85 (s, 1H); ^{13}C NMR: δ 16.1 (q), 19.4 (q), 28.0 (q), 29.1 (t), 36.2 (t), 44.0 (s), 45.8 (d), 51.0 (q), 51.4 (q), 59.9 (d), 62.0 (s), 102.1 (s), 171.5 (s), 176.5 (s), 180.6 (s); *m/e* 282 (4%). Calc. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85; found: C, 63.75; H, 7.80%. Compound **23** could be separated in similar yield from **24** and **25** by medium pressure liquid chromoatography with 9 : 1 hexanes/ethyl acetate (v/v) as eluent.

2 - syn - 8 - *Dicarbomethoxy* - 4,4 - *dimethylbicyclo*[3.2.1]*oct* - 2 - *en* - 3 - *ol* (**24**) *and* 2 - anti - 8 - *Dicarbomethoxy* - 4,4 - *dimethylbicyclo*[3.2.1]*oct* - 2 - *en* - 3 - *ol* (**25**).[54] Lithium wire (63 mg, 9.1 mg-atom) was added to a stirred solution of **22** (496 mg, 1.86 mmol) in ether (13 ml) and ammonia (15 ml) under nitrogen. After 1.5 hr all the lithium metal appeared to have reacted. Solid ammonium chloride was added and the ammonia was allowed to evaporate. Saturated aq ammonium chloride (10 ml) was added, followed by sufficient water to dissolve all the salts. The layers were separated and the aqueous phase was extracted with ether (3 × 10 ml). The combined organic layers were dried and concentrated to give a colorless oil (321 mg) containing a ~1 : 1 mixture of **24** and **25**. Separation by medium pressure liquid chromatography using hexanes/ethyl acetate (9 : 1 v/v) as eluent, gave **25** (108 mg, 0.40 mmol, 22%) and **24** (97 mg, 0.36 mmol, 19%).

Crystallization of **24** from a mixture of pentanes and ethyl acetate gave white crystals, m.p. 113–114.5°; λ_{max} 5.78, 6.08, 6.23 μ; ^{1}H NMR: δ 1.13 (s, 3H), 1.19 (s, 3H), 1.38–2.14 (m, 4H), 2.40 (m, 1H), 2.67 (t, J = 4 Hz, 1H), 3.24 (m, 1H), 3.64 (s, 3H), 3.81 (5, 3H), 12.15 (s, 1H); ^{13}C NMR: δ 25.3 (q), 26.1 (t), 27.4 (q), 32.3 (t), 34.4 (d), 40.5 (s), 48.6 (d), 49.3 (d), 51.1 (q), 51.6 (q), 102.1 (s), 172.4 (s), 173.4 (s), 175.7 (s); *m/e* 268 (72%). Calc. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51; found: C, 62.73; H, 7.49%. Similarly, crystallization of **25** from a mixture of pentanes and ethyl acetate gave

white crystals, m.p. 82–83.5°; λ_{max} 5.78, 6.08, 6.23 μ; ^{1}H NMR: δ 1.20 (s, 3H), 1.29 (s, 3H), 1.58–2.07 (m, 4H), 2.33 (m, 1H), 2.86 (s, 1H), 3.30 (m, 1H), 3.71 (s, 3H), 3.78 (s, 3H), 12.11 (s, 1H); ^{13}C NMR: δ 23.0 (t), 23.3 (q), 27.9 (q), 31.8 (d), 36.8, 42.6 (s), 48.5 (d), 49.5 (d), 51.5 (q), 51.7 (q), 103.4 (s), 172.1 (s), 174.0 (s), 177.5 (s); *m/e* 268 (46%). Calc. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51; found: C, 62.70; H, 7.51%.

1 - *Carbomethoxy* - 4,4 - exo - 8 - *trimethyl* - cis - *bicyclo*[3.3.0]*octan* - 3 - *one* (**35**). A mixture of **23** (1.33 g, 4.72 mmol) and sodium chloride (300 mg, 5.13 mmol) was stirred and heated (120°) in reagent grade dimethyl sufoxide (5.0 ml) containing added water (100 μl, 5.56 mmol) for 10 hr under nitrogen. After cooling, the mixture was diluted with water (20 ml) and extracted with pentane (5 × 10 ml). The combined pentane extracts were washed with water (3 × 10 ml), dried, and concentrated. The residual oil was molecularly distilled (65°, 0.2 mm) to give **35** (786 mg, 3.51 mmol, 74%) as a colorless, mobile oil: λ_{max} 5.78 μ; ^{1}H NMR: δ 0.94 (d, J = 6 Hz, 3H), 0.99 (s, 6H), 1.16–2.10 (m, 5H), 2.09 (d, J = 20 Hz, 1H), 2.65–3.02 (m, 1H), 3.35 (d, J = 20 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR: δ 15.4 (q), 19.2 (q), 27.4 (q), 29.2 (t), 34.6 (t), 45.9 (t), 49.0 (s), 49.1 (d), 51.8 (q), 55.6 (s), 57.2 (d), 176.6 (s), 220.1 (s); *m/e* 224 (42%). Calc. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99; found: C, 69.41; H, 8.93%.

1 - *Carbomethoxy* - exo - 3 - *ethyl* - 4,4 - exo - 8 - *trimethyl* - cis - *bicyclo*[3.3.0]*octan* - 3 - *ol* (**39**).[54] A solution of lithium acetylide in tetrahydrofuran was rprepared by bubbling acetylene gas (dried by passage through a dry ice/acetone cold trap[55]) into a cold (−75°), stirred solution of n-butyllithium (2.66M in hexane; 52 ml, 13.8 mmol) in tetrahydrofuran (15 ml). The system was flushed with nitrogen, and a solution of **35** (631 mg, 2.82 mmol) in tetrahydrofuran (5 ml) was added. The resulting clear, colorless solution was stirred at −75° for 0.5 hr and was then allowed to warm to 10°. Saturated aq ammonium chloride (20 ml) was added and the phases were separated. The aqueous phase was extracted with ether (3 × 10 ml). The organic phases were combined, washed with saturated aq sodium chloride, dried, and concentrated to give a colorless oil. A ^{1}H NMR spectrum of this material indicated it to be a mixture of **39** and **35** in a ratio of ~7 : 3. Repeated crystallization of this oil from hexanes containing 5–10% ethyl acetate gave **39** (430 mg, 1.72 mmol, 61%). Further recrystallizations from the same solvent system gave **39** as white plates, m.p. 95–96°; λ_{max} 2.79 (m), 3.03 (m), 5.81 μ; ^{1}H NMR: δ 0.87 (d, J = 7 Hz, 3H), 1.00 (s, 3H), 1.07 (s, 3H), 1.23–2.33 (m, 6H), 2.03 (d, J = 14 Hz, 1H), 2.47 (s, 1H), 2.53–2.91 (m, 1H), 2.81 (d, J = 14 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR: δ 14.6 (q), 17.5 (q), 29.1 (q), 29.2 (t), 35.3 (t), 47.4 (t), 47.8 (d), 48.0 (s), 51.4 (q), 60.0 (d), 61.3 (s), 73.0 (d), 81.9 (s), 85.3 (d), 177.8 (s); *m/e* 250 (2%). Calc. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86; found: C, 71.79; H, 8.75%.

1 - *Carbomethoxy* - 3 - (1 - *oxoethyl*) - 4,4 - exo - 8 - *trimethyl* - cis - *bicyclo*[3.3.0]*oct* - 2 - *ene* (**40**). A solution of propargylic alcohol **39** (230 mg, 0.92 mmol) in anhydrous formic acid (8.5 ml) containing concentrated sulfuric acid (0.5 ml) was stirred and heated (90°) for 15 min. After cooling to room temperature, the solution was poured into a mixture of water (20 ml) and ether (30 ml). The layers were separated and the aqueous phase was extracted with ether (3 × 10 ml). The combined organic layers were washed with water (3 × 10 ml), saturated aq sodium bicarbonate (10 ml), and saturated aq sodium chloride (10 ml). The solution was dried and concentrated to leave a dark brown oil (169 mg). Preparative thin layer chromatography with CH_2Cl_2 as eluent gave 40 (100 mg) in a band of R_f 0.29. Molecular distillation (65°/0.025 mm) gave **40** (65 mg, 0.26 mmol, 28%) as a colorless, mobile oil; λ_{max} 5.82, 6.00, 6.20 (w), 7.37 μ (m); ^{1}H NMR: δ 1.00 (d, J = 6 Hz, 3H), 1.14 (s, 3H), 1.19 (s, 3H), 1.25–2.30 (m, 5H), 2.29 (s, 3H), 2.79 (m, 1H), 3.70 (s, 3H), 6.56 (s, 1H); ^{13}C NMR: δ 15.8 (q), 21.7 (q), 28.1 (q), 28.3 (t), 30.5 (q), 35.1 (t), 45.3 (d), 46.9 (t), 51.6 (q), 59.9 (d), 67.3 (s), 144.0 (d), 149.2 (s), 174.9 (s), 197.3 (s); *m/e* 250 (47%). Calc. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86; Found: C, 71.43; H, 8.91%; *m/e* 250.1562; MW 250.1569.

In a similar experiment, **39** (65 mg, 0.26 mmol) was stirred and heated (104°) for 1 hr in a solution of 92% formic acid (6.7 ml) containing concentrated sulfuric acid (1 drop/5 ml). Workup gave a brown oil (63 mg) which was chromatographed on a 0.25 mm silica gel plate eluted with CH_2Cl_2. Compounded **40** (21 mg, 0.08 mmol, 30%) was found in a band at R_f 0.35, while **41** (16 mg, 0.07 mmol, 27%) was found at R_f 0.63. Molecular distillation (50°/0.1 mm) gave **41** as a colorless oil; λ_{max} 3.13 (m), 4.78 (w), 5.82 μ; ^{1}H NMR: δ 0.90 (d, J = 7 Hz, 3H), 1.28 (s, 3H), 1.15–2.57 (m, 6H), 1.75 (d, J = 1.5 Hz, 3H), 2.27 (s, 1H), 2.93 (m, 1H), 3.70 (s, 3H); *m/e* 232 (25%). Calc. for $C_{15}H_{20}O_2$; MW 232.1463; found: *m/e* 232.1452.

1 - *Carbomethoxy* - exo - 3 - (1 - *oxoethyl*) - 4,4 - exo - 8 - *trimethyl* - cis - bicyclo[3.3.0]octan - 3 - ol (**45**). A mixture of propargylic alcohol **81** (169 mg, 0.68 mmol) and mercuric sulfate (232 mg, 0.78 mmol) was stirred and heated at reflux for 2 hr under nitrogen in 95% ethanol (20 ml) containing concentrated sulfuric acid (2 drops). After cooling to room temperature, a spatula tip of sodium bicarbonate was added and the mixture was evaporated to dryness. Magnesium sulfate was added and the residual solids were washed thoroughly with chloroform. The washings were stripped of solvent and the residue was sublimed (95°/0.01 mm) to give **45** (131 mg, 0.49 mmol, 72%). Thin layer chromatography with cyclohexane/ethyl acetate as eluent (1 : 1 v/v) gave **45** in a band at R_f 0.51. Sublimation (71°/0.15 mm) gave **45**, m.p. 89–91°; λ_{max} 2.94 (m), 5.85, 5.90 (sh), 7.41 μ (m); ^{1}H NMR: δ 0.90 (d, J = 7 Hz, 3H), 0.92 (s, 3H), 0.96 (s, 3H), 1.45–2.45 (m, 5H), 1.82 (d, J = 14.5 Hz, 1H), 2.27 (s, 3H), 2.66 (t, J = 9 Hz, 1H), 3.14 (dd, J = 14.5 Hz, J = 1.5 Hz, 1H), 3.38 (d, J = 1.5 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR: δ 14.5 (q), 17.7 (q), 28.0 (q), 28.7 (q), 29.2 (t), 35.1 (t), 42.3 (t), 47.6 (d), 48.4 (s), 51.5 (q), 61.6 (s), 61.9 (d), 91.6 (s), 178.1 (s), 211.9 (s); *m/e* 268 (2%). Calc. for $C_{15}H_{24}O_3$: C, 67.14; H, 9.01; found: C, 67.24; H, 9.00%.

endo - 3 - *Acetoxy* - 1 - *carbomethoxy* - exo - 3 - (1 - *oxoethyl*) - 4,4 - exo - 8 - *trimethyl* - cis - *bicyclo*[3.3.0]*octane* (**46**). Acetic anhydride (140 μl, 151 mg, 1.48 mmol) was added to a stirred solution of **45** (99 mg, 0.37 mmol) and 4-N,N-dimethylaminopyridine (181 mg, 1.48 mmol) in dichloromethane (1.0 ml) under nitrogen. After being stirred at room temperature for 14 hr, the pale yellow reaction solution was diluted with ether (20 ml). The resulting solution was washed with 10% hydrochloric acid (2 × 10 ml), saturated aq sodium bicarbonate (10 ml), and saturated aq sodium chloride (10 ml), dried, and concentrated to give 46 (110 mg, 0.35 mmol, 95%). Preparative thin layer chromatography with 2 : 1 cyclohexane/ethyl acetate (v/v) as eluent gave **46** in a band at R_f 0.51; molecular distillation (80°/0.02 mm) gave **46** as a colorless, viscous oil; λ_{max} 5.82 μ; ^{1}H NMR: δ 0.79 (s, 3H), 0.90 (d, J = 6.5 Hz, 3H), 1.16 (s, 3H), 1.4–2.2 (m, 5H), 2.11 (s, 6H), 2.16 (d, J = 16 Hz, 1H), 2.58–2.97 (m, 1H), 3.41 (d, J = 16 Hz, 1H), 3.71 (s, 3H); *m/e* 311 (M + 1, 29%). Calc. for $C_{17}H_{26}O_5$: C, 65.78: H, 8.44; found: C, 65.94; H, 8.38%.

1 - *Carbomethoxy* - endo - 3 - (1 - *oxoethyl*) - 4,4 - exo - 8 - *trimethyl* - cis - *bicyclo*[3.3.0]*octane* (**47**). Compound **40** (25 mg, 0.10 mmol) was hydrogenated at atmospheric pressure in ethyl acetate (5 ml) over platinum (formed from platinum oxide *in situ*; 25 mg) for 6 hr. The catalyst was filtered and the filtrate was concentrated to give **47** (21 mg, 0.08 mmol, 80%) as a colorless, mobile oil. Purification was accomplished by thin layer chromatography with cyclohexane/ethyl acetate (2 : 1 v/v) as eluent (R_f 0.56) and molecular distillation (70°/0.1 mm); λ_{max} 5.83, 7.27 μ (m); ^{1}H NMR: δ 0.80 (s, 3H), 0.92 (d, J = 6 Hz, 3H), 1.12 (s, 3H), 1.0–2.2 (m, 6H), 2.14 (s, 3H), 2.35–2.85 (m, 3H), 3.69 (s, 3H); *m/e* 250 (21%). Calc. for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59; found: C, 71.63; H, 9.57%.

(±) - exo - 2,6,6 - *Trimethyltricyclo*[5.3.1.0^{1,5}]*undecane* - 8,10 - *dione* (**11**).[54] Compound **47** (21 mg, 0.08 mmol) was added to a solution prepared by heating potassium (54 mg, 1.38 mg-atom) in boiling tert-butyl alcohol (1.5 ml), and the mixture was boiled under reflux for 1.5 hr. The solution was then cooled to room temperature, diluted with water (10 ml), and washed with ether (4 × 5 ml). The aqueous solution was made strongly acidic by the addition of concentrated hydrochloric acid (1 ml), producing a fine white precipitate. The resulting mixture was extracted with chloroform (3 × 10 ml), which slowly removed the precipitate. The chloroform extracts were combined, dried, and concentrated to give **11** (18 mg, 0.08 mmol. ~100%) as an off-white solid. Recrystallization from a mixture of dioxane and pentane gave **11** (8 mg) as white crystals, m.p. 177.5–179°: λ_{max} 5.81 (sh), 5.88 μ;

^{1}H NMR: δ 1.07 (*s*, 3*H*), 1.12 (*s*, 3*H*), 1.25 (*d*, J = 6 Hz, 3H), 1.4–2.5 (m, 8H), 2.62 (m, 1H), 3.25 (s, 2H); ^{13}C NMR: δ (NaOH/D_2O) 18.6 (q), 29.7 (q), 29.9 (t), 31.4 (q), 42.6 (t), 43.9 (s), 46.9 (d), 47.5 (d), 64.6 (d), 67.1 (s), 67.4 (d), ~ 105, 203.8 (s), 211.1 (s);[56] *m/e* 220 (39), 192 (45), 178 (15), 177 (59), 176 (6), 174 (8), 165 (9), 164 (36), 163 (21), 161 (11), 159 (14), 150 (43), 149 (100), 145 (10), 137 (13), 136 (22), 135 (42), 134 (26), 133 (13), 125 (15), 123 (22), 122 (31), 121 (56), 119 (21), 109 (37), 108 (25), 107 (73), 105 (22), 95 (21), 94 (20), 93 (41), 92 (10), 91 (45), 83 (36), 81 (23), 80 (10), 79 (38), 78 (8), 77 (30). Calc. for $C_{14}H_{20}O_3$: 220.1463; found: 220.1465.

The spectra were identical with those of optically-active **11**.[8,52,57]

Acknowledgement—We thank the Natural Sciences and Engineering Research Council of Canada for support of this work.

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[57]We thank Dr Martin Smith, Bruker Spectrospin (Canada) Ltd. for the ^{13}C NMR spectroscopic comparison of (±)-**11** and optically-active **11**.