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Synthesis of (±)-Lineatin, an Aggregation Pheromone Component of *Trypodendron lineatum*

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An efficient six-step synthesis of racemic lineatin (*1*) by two analogous routes is described. The key reaction is a thermal intramolecular allene-ene cycloaddition reaction. In connection with other strategies toward lineatin the thermal cycloadditions of dichloroketene to 2,5,5-trimethylcyclopentadiene and the photochemical addition of ketene acetals to methyl substituted cyclopentenones have been studied.

The ambrosia beetle, *Trypodendron lineatum* (L.), is a serious pest to coniferous forests in Europe and North America. In 1977 Silverstein and co-workers[1] isolated an aggregation pheromone component, lineatin (*1*), produced by the female beetle. They proposed one of two isomeric tricyclic acetals as the structure, and the correct one was established by synthesis.[2] Subsequently other more efficient syntheses have been published[3–8] some of them also leading to optically active lineatin[4,5,7] and the absolute configuration was established.[7] It has been found that (+)-*1* is a pheromone component of other *Trypodendron* species as well.[9] For practical purposes the preparation of racemic *1* is satisfactory since no adverse biological effects have been observed for the (−)-enantiomer.[10]

Field tests have demonstrated[10,11] the potential of the pheromone as a tool for controlling the pest and a need for larger quantities of the active principle was apparent. The present paper reports our work which leads to a practical synthesis of (±)-lineatin. A preliminary communication on part of this work has been published.[12]

RESULTS AND DISCUSSION

Contrary to previously reported strategies for the synthesis of *1*, our retrosynthetic analysis led to the allenic ketone *5* (Scheme 1). A thermally induced intramolecular cycloaddition of *5* should yield the bicyclic ketone *7*, which contains the substituents and functionality required for a successful transformation to (+)-*1*.

Reactions of the readily available[13,14] allenic aldehydes *2* with β-methallylmagnesium chloride furnished the alcohols *3*; using an excess of Grignard reagent in ether at 0 °C, 90 % yields were obtained. Under these conditions a small amount (~1 %) of 4,4,7,7-tetramethyl-1,2,8,9-decatetraen-5-one (*4*) was formed. The amount of the by-product increased with reaction temperature becoming the major product at reflux temperature together with some 2,2-dimethyl-3,4-pentadien-1-ol[15] and unreacted aldehyde. The results were not improved by replacing ether with THF as solvent. The diallene *4* probably results

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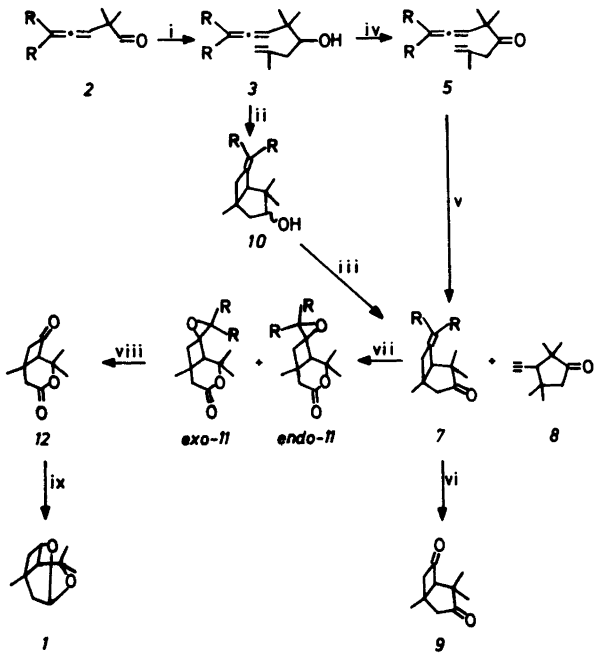


Scheme 1. a, R=H; *b,* R=CH_3.

(i) CH_2=C(Me)MgCl/Et_2O/0 °C/4h; (ii) 430–450 °C/0.2 mmHg; (iii) $H_2Cr_2O_7$/Me_2CO; (iv) $H_2Cr_2O_7$/Et_2O/2–3 days; (v) 490 °C/1–2 mmHg; (vi) O_3/CH_2Cl_2/MeOH/Me_2S; (vii) mCPBA/$NaHCO_3$/CH_2Cl_2; (viii) H_5IO_6/Et_2O; (ix) DIBAH/hexane/Et_2O/–60 °C or $LiAl(OBu^t)_3H$/Et_2O

from reductive dimerization of the aldehyde *2a* followed by dehydration of the initially formed diol.

The oxidation of an etheral solution of *3* with chromic acid was slow at room temperature. The solvent was actually oxidized at a rate comparable with that of the alcohol and a large excess of oxidizing agent was therefore required in order to ensure complete conversion of *3*. The portionwise addition of between two and four equivalents of chromic acid to a concentrated (2–3 M) solution of the alcohol *3a* in ether at 12–18 °C during a period of 70–100 h afforded the ketone *5a* in 90 % yield. By the same procedure *3b* was oxidized to *5b* also in 90 % yield but at a somewhat faster rate. The reaction could advantageously be carried out on the crude alcohols but it should be noted that the olefin 2,5-dimethyl-1,5-hexadiene, an unvaoidable by-product from the preparation of the Grignard reagent, apparently promotes the acid-catalyzed allene-acetylene isomerization of the ketone *5a* to *6*. Changing the solvent to CH_2Cl_2 caused no improvement since a number of unidentified by-products were formed lowering the yield of *5a* to 76 %. Lower yields of the ketones were also obtained with the Jones oxidation procedure which was slow and required an excess of reagent as well.

The precedence for the intramolecular cycloaddition step was provided by an earlier observation [16] that the thermal gas phase reaction of the allene 1,2,7-octatriene led to a 1:1 mixture of bicyclo[4.2.0]octene and 6-methylenebicyclo[3.2.0]heptane. In a similar way, distillation of *5a* at 0.5–2.0 mmHg through a quarts tube packed with quarts wool and kept

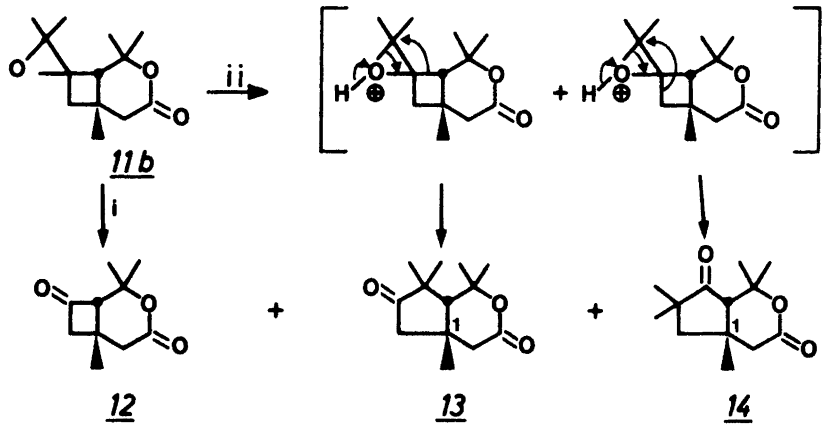
between 480–500 °C furnished a 3:1 mixture of the desired bicyclic ketone *7a* and the isomeric acetylenic ketone *8* as major products. These reaction conditions were quite critical; at lower temperatures and pressure the conversion decreased, while at higher temperatures or pressure both the number and amounts of other products increased. On the other hand, the ratio *7a*:*8* was not influenced significantly by changes of either temperature or pressure. The isomers could not be separated conveniently by distillation or chromatography; however, the ketone *8* was precipitated quantitatively from the crude reaction mixture as the silver acetylide using $AgNO_3$ in ethanol.[17] Distillation of the filtrate afforded the ketone *7a* in 45 % yield and *8* was obtained by hydrolysis of the silver acetylide with aqueous NaCN.

The spectral properties of *8* were consistent with the assigned structure. On the basis of spectroscopic evidence alone the structure of *7a* appeared quite sound as well. In the 400 MHz ^{1}H NMR spectrum the two olefinic protons appear as a quartet. Double resonance experiments reveal geminal coupling, coupling with the bridgehead proton and with one of the protons at C-7, with similar coupling constants for all. The bridgehead proton is also coupled with one of the protons at C-7; the magnitude, 2.4 Hz, of the 1,3-coupling is not unusual for cyclobutanes.[18] Conclusive structural evidence for *7a* was obtained from X-ray analysis[19] on the diketone *9*, the product of ozonolysis. The analogous thermal reaction of *5b* gave also a mixture of products but the major component, *7b*, was obtained in 51 % yield by distillation through an efficient column. Most of the minor products have been separated and identified. This work as well as a study on the formation of *8* will be reported in due course.[20] Finally, the thermal reaction of the alcohol *3a* at 430 °C gave a complex mixture of products from which 6-methylene-1,4,4-trimethylbicyclo[3.2.0]heptan-3-ol (*10*) could be identified by its oxidation to the ketone *7a*. Compound *10* constituted less than 20 % of the mixture.

It is known[21,22] that [2+2]cycloaddition reactions involving allenes are catalyzed by Lewis acids. We treated the alcohol *3a* with CuCl, $CuSO_4$ or $ZnCl_2$ in THF or DMF at reflux temperatures but no reaction was observed even after 69 h. On the other hand, reactions of the ketones *5a* and *5b* with $AlBr_3$ in chlorobenzene resulted in complex mixtures of which the bicyclic ketones *7a* and *7b* constituted only a few percent according to GLC analysis.

The oxidiation of *7* using *m*-chloroperbenzoic acid in CH_2Cl_2 in the presence of $NaHCO_3$ gave the epoxylactones *11*. GLC analysis on a 25 m capillary column revealed that *11a* consisted of a 88:12 mixture of stereoisomers while in the case of *11b* the ratio was 95:5. Steric effects suggest that the oxirane ring of the major isomers should be *exo* oriented. The stereoisomers could not be separated but the spectroscopic data of *11a* are in agreement with this supposition. In its ^{1}H NMR spectrum one of the protons of the oxirane methylene group appears as a doublet at δ 3.24 ppm for the major isomer and at 3.62 ppm for the minor one. Examining a model of *11a* it becomes apparent that the six-membered lactone ring can attain several conformations; however, the oxirane methylene group of the *exo* isomer will experience either the shielding effect of the methyl group (at position 5) or the anisotropic shielding effect of the carbonyl group. Hence, the resonance due to the oxirane methylene group of the *exo* isomer should appear at higher field than of the *endo* isomer. Due to the additional steric hindrance by the *gem*-dimethyl groups at the double bond of *7b*, it is reasonable that the *exo*-isomer of *11b* should be formed even more predominantly.

The oxidation of epoxides to ketones is known to proceed smoothly with H_5IO_6[23], and *11a* reacted quantitatively and exothermally to the known ketolactone *12*,[4,6,2] which was purified by recrystallization. Unfortunately the epoxide *11b* furnished *12* in only 75 % yield



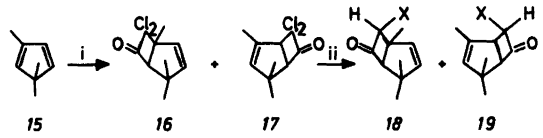
Scheme 2. (i) H_5IO_6/Et_2O; (ii) 88 % aqueous HCO_2H.

together with the minor products *13* (14 %) and *14* (11 %). Compound *13* was obtained crystalline and the structure shown by X-ray crystallography [19] to be 1,5,5,7,7-pentamethyl-4-oxabicyclo[4.3.0]nona-3,8-dione. Selective formation of the 2,4-dinitrophenylhydrazones of *12* and *13*, followed by chromatography of the mother liquor afforded 1,5,5,8,8-pentamethyl-4-oxabicyclo[4.3.0]nona-3,7-dione (*14*) as a liquid. Both isomeric ketones *13* and *14* result from acid catalyzed rearrangement of the oxirane *11b* (Scheme 2). Accordingly, the treatment of *11b* with 88 % aqueous formic acid produced a complex mixture containing both *13* and *14* as shown by GLC-analysis, and *13* was isolated from the mixture as well.

Little is known about the mechanism of the periodic acid oxidation, although an intermediate cyclic periodate ester has been proposed.[24] Following the reactions of *11a* or *11b* by GLC, both stereoisomers of the epoxides disappeared within minutes while very little of *12* was formed. The epoxides were reformed when aliquotes of the reaction mixture were treated with a few drops of saturated $NaHCO_3$ solution. Moreover, *endo-11* produces *12* at a much faster rate than the *exo*-isomers, which need several hours at room temperature for complete conversion. These results indicate that the reaction is initiated by a reversible acid catalyzed opening of the oxirane ring. Assuming cyclic esters are involved, formation of these will have to be the rate determining step. It would explain the higher rate of oxidation observed for the *endo* isomers of *11*, which should form the sterically least crowded cyclic esters.

The transformation of the ketolactone *12* to lineatin (*1*) has been carried out using diisobutylaluminium hydride (DIBAH) followed by acidification.[4,6] The high volatility of *1* caused significant loss of material upon chromatography and evaporation of solvents and yields below 30 % were reported. In our case the use of chromatography was unnecessary and by modifying the published isolation procedure [6] lineatin was obtained in 74 % yield. The same yield of *1* was arrived at with tri-*t*-butoxyaluminium hydride in ether as reducing agent and this is actually the method of choice for this step of the synthesis. On a larger scale the prolonged distillation time caused formation of high boiling material and lower yield of *1*. This problem was solved by using short path distillation equipment.

Other strategies for the synthesis of *1* were tried. None of them led to a successful



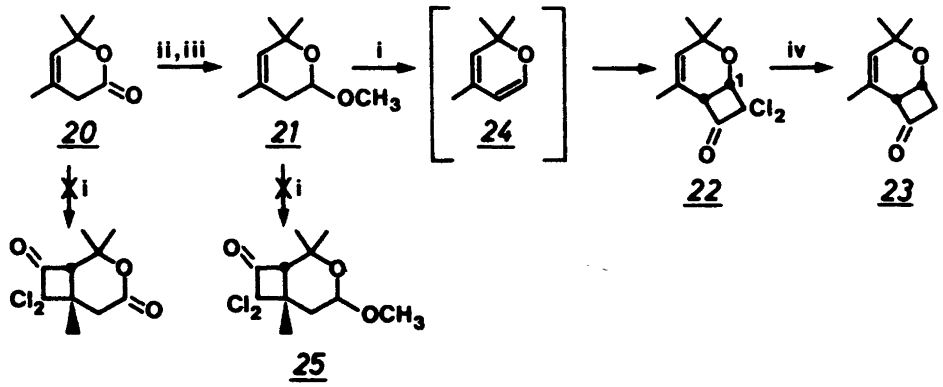
Scheme 3. *a*, X=H; *b*, X=Cl.

(i) $Cl_2CHCOCl/Et_3N$/pentane/Δ; (ii) Zn/HOAc.

synthetic route, but we want to report some results from intermolecular [2+2] cycloaddition reactions which were initial steps in these schemes.

Dichloroketene, generated from dichloroacetyl chloride and triethylamine, underwent additon to 2,5,5-trimethylcyclopentadiene (*15*) affording the isomeric adducts *16* and *17* as a 1:1 mixture in 26 % yield (Scheme 3). We were not able to separate the isomers but the structures were assigned from the spectral data recorded on the mixture. Dehalogenation of *16* and *17* with zinc in acetic acid gave a mixture of *18a* and *19a* which could be separated by preparative GLC. The cyclobutanone moiety was evident from the absorption in the IR at 1790 and 1785 cm^{-1}, respectively. The ^1H NMR spectrum of *18a* shows three singlets due to the methyl groups, two overlapping singlets for the three protons α to the carbonyl group and a characteristic AB pattern for the olefinic protons. In the case of *19a* the ^1H and ^{13}C NMR spectra do not unambiguously distinguish between the two possible regioisomers. The coupling between protons across the cyclobutanone ring complicates the matter; for the *endo*-monochloro adducts[25] *18b* and *19b* these coupling constants are actually 2.75 and 3.0 Hz, respectively. However, by analogy with previous[26] results from similar addition reactions we assume *19a* to be the correct structure. It is interesting to note that the two double bonds of *15* are equally reactive while tri-substituted open-chain alkenes have been reported[27,28] as practically unreactive toward dichloroketene generated by this method.

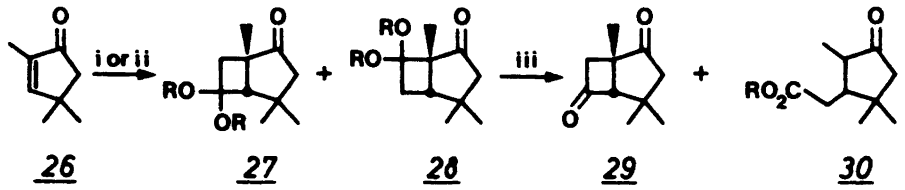
The lactone *20* is easily prepared[5] and appeared to be a most convenient starting material for the synthesis of *1* (Scheme 4). Unfortunately, no reaction took place with dichloroketene, generated by any of the three methods tried;[26,28] only isomerization to the α,β-unsaturated lactone was observed. The low reactivity of *20* in this reaction has been experienced by others as well.[29] Since the lack of reactivity might be caused by the carbonyl



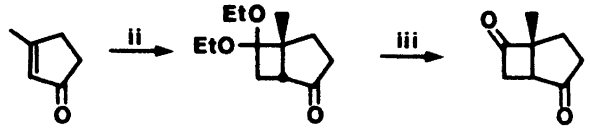
Scheme 4. (i) $Cl_2C{=}C{=}O$; (ii) $LiAlH_4$/THF; (iii) $HC(OCH_3)_3/CH_3OH$; (iv) Bu_3SnH.

group the lactone *20* was transformed into the acetal *21*. Reaction of the latter with dichloroketene by the method of Hassner[28] gave 7,7-dichloro-2,4,4-trimethyl-5-oxabicyclo[4.2.0]oct-2-en-8-one (*22*) as sole product in 45 % yield. The same compound was also formed using the method of Brady[27] albeit in only 6 % yield. The structure was established on the basis of spectroscopic evidence which was also compared with that obtained for the dehalogenated compund *23*. In particular, the bridgehead proton adjacent to oxygen appears as a doublet in the ^{1}H NMR spectrum of *22* while the resonance for the analogous proton in *23* shows up as an octet. This is compatible with the assigned structures but not with those of the regioisomer. The formation of *22* can only be rationalized if elimination of methanol from the acetal *21* precedes the addition of dichloroketene. It was expected that $ZnCl_2$, present in the reaction mixture, would catalyze the elimination and that the pyran *24* would react readily with dichloroketene. Support for this path was obtained from a reaction of *21* with $ZnCl_2$ in ether which gave the pyran *24* and the corresponding ring opened product 3,5-dimethyl-2,4-hexadieneal. It has previously been reported[2] that the addition of dichloroketene to *21* gave the desired adduct *25* in 5 % yield. We have not been able to detect this compound in our reaction mixtures.

The photochemical addition of ketene acetals to α,β-unsaturated ketones has been reported[30] to give the "head-to-tail" products in a highly regio- and stereoselective manner. Contrary to these reports we obtained mixtures of the two possible regioisomers when ketene acetals were added to 2,4,4-trimethylcyclopent-2-enone (*26*) (Scheme 5). In the case of ketene dimethylacetal a 71:29 mixture of the adducts *27a* and *28a* was isolated in 73 %



26 *27* *28* *29* *30*



31 *32* *33*

Scheme 5. a, R=CH_3; *b*, R=C_2H_5.

(i) $=\langle^{OCH_3}_{OCH_3}$/pentane/*hv*; (ii) $=\langle^{OC_2H_5}_{OC_2H_5}$/pentane/*hv*; (iii) HCl/H_2O.

yield, and a 67:33 mixture of the corresponding adducts *27b* and *28b* was obtained in 58 % yield employing the diethylacetal. The compounds *27a* and *28a* were separated by preparative GLC and their structures established from spectral evidence. In the ^{1}H NMR spectra of both isomers three methyl and two methoxy singlets can be distinguished. In the spectrum of *27a* the two methylene protons appear as four doublets and the methine proton as a singlet while in the spectrum of *28a* they appear as a complex absorption. In the ^{13}C NMR spectra the downfield shift of the bridgehead C-5 carbon of *27a* compared with *28a* confirms the depicted structures. The structures of *27b* and *28b* were established by comparing the ^{13}C NMR spectrum of the mixture with the spectra of *27a* and *28a*. The adducts were hydrolyzed with aqueous hydrochloric acid to the expected diketone *29* and the keto esters *30* which were separated by preparative GLC. The IR spectrum of *29* exhibits absorptions at 1790 and 1745 cm^{-1} indicative of carbonyl groups of four- and five-membered rings, respectively. The ^{1}H NMR spectrum shows three singlets due to the methyl groups and resonances characteristic of protons α to carbonyl groups. The ^{13}C NMR spectrum confirms the structure. Both keto esters *30a* and *30b* exhibit carbonyl absorptions at 1745 cm^{-1} in the IR. The ^{1}H NMR spectra are in agreement with the structures and also show that the two compounds have been formed as mixtures of stereoisomers. The ^{13}C NMR spectra exhibit absorptions characteristic of all the carbon atoms of compounds *30a* and *30b*, respectively. It seems reasonable that the keto esters are formed by a *retro* Claisen-type reaction of the intermediate hemiacetal. The relatively low regioselectivity observed for these cycloaddition reactions has a reasonable explanation in the steric effect of *gem* dimethyl groups. In support of this notion, the photochemically induced reaction of ketene diethylacetal to 3-methyl-2-cyclopentenone (*31*), gave only the "head-to-tail" isomer *32* in 53 % yield. It was hydrolyzed to the diketone *33* and both components were characterized by spectroscopic data.

In conclusion, the preparation of (±)-lineatin (*1*) on a multigram scale has been accomplished by the sequence of reactions outlined in Scheme 1. The overall yield of *1* is slightly better starting from the allenic aldehyd *2a* (27 %) than from *2b* (23 %). The use of the latter as starting material avoids the somewhat cumbersome separation of the acetylene *8* and may well be the choice for a large-scale preparation. The ketolactone *12* offers itself as a convenient substrate for the preparation of the enantiomers of lineatin and work towards this goal is in progress.

EXPERIMENTAL

General. GLC analyses were performed with a packed 2.4 m column of 3 or 10 % SP2100 if not otherwise mentioned. IR spectra were recorded on a Perkin-Elmer 281B instrument. Routine NMR spectras were recorded on Varian EM360A, Jeol JNMFX60 or Varian V-3521A. 200 MHz spectras were recorded on Bruker CXP-200 and 400 MHz spectras on Bruker WM-400. Fractional distillation was carried out through a Fisher Spalt-rohr HMS 300 with 90 theoretical plates. The photochemical reactions were performed with a 250 W immersion high pressure mercury lamp with a pyrex filter. MS spectra were recorded on GC/MS VG micromass 7070F. If not otherwise stated the *m/z*-values are given for chemical ionisation with isobutane.

Materials. Commercially available starting materials and solvents were purified and dried when necessary by usual methods. 2,5,5-trimethylcyclopentadiene (*15*),[31] 4,6,6-trimethyl-3,6-dihydro-2*H*-pyran-2-one (*20*),[32] 2,2,4-trimethyl-6-methoxy-5,6-dihydro-2*H*-pyran (*21*),[5] 2,4,4-trimethyl-2-cyclopentenone (*26*),[4] 3-methyl-2-cyclopentenone (*31*),[33] ketene dimethylacetal[34] and ketene diethylacetal[35] were prepared according to literature procedures.

2,2-dimethyl-3,4-pentadienal (2a), was prepared in 39 % yield from propargyl alcohol and isobutyric aldehyde in tetralin or 1,3-diisopropylbenzene solution with p-toluenesulfonic acid as catalyst according to the lit.[13]

2,2,5-trimethyl-3,4-hexadienal (2b), was prepared in 50 % yield from 2-methyl-3-butyn-2-ol and isobutyric aldehyde in benzene with a catalytic amount of *p*-toluenesulfonic acid according to the lit.[14], b.p. 103 °C/100 mmHg (lit.[14] 96–99 °C/104 mmHg). The improvement from that reported (38 %) was obtained by extending the reaction time to 100 h.

General procedure for the synthesis of 3. To a mixture of Mg (0.30 mol) in 300 ml dry ether kept below 10 °C was added β-methallyl chloride (0.30 mol) during 15 min and the mixture was stirred vigorously at this temperature overnight. The white suspension was cooled to 0 °C and *2* (0.10 mol) in 150 ml dry ether was added dropwise with stirring during 1 h. The mixture was stirred at 0 °C until all of the aldehyde was consumed (GLC). Saturated NH_4Cl (aq., 37 ml) was added with vigorous stirring. The organic phase was decanted from the precipitated magnesium salts which were washed several times with ether. Evaporation of the ether extract followed by distillation gave the alcohols *3*.

2,5,5-trimethylocta-1,6,7-trien-4-ol (3a), b.p. 60–61 °C/1.5 mmHg. ^{1}H NMR (60 MHz, CCl_4): δ 1.02 (s, 6 H), 1.53 (broad s, 1 H), 1.73 (broad s, 3 H), 1.9–2.2 (m, 2 H), 3.30 (dd, *J* 3 Hz, 10 Hz, 1 H), 4.6–5.2 (complex abs., 5 H). IR (film): 3580 (m), 3490 (m), 3050 (m), 1960 (s), 1653 (m), 1395 (m), 1382 (m) cm^{-1}. Yield 91 %.

2,5,5,8-tetramethylnona-1,6,7-trien-4-ol (3b), b.p. 61–62 °C/0.3 mmHg, n_D^{16} 1.4810. ^{1}H NMR (60 MHz, CCl_4): δ 0.95 (s, 6 H), 1.5–2.4 (complex abs., 11 H), 2.98 (broad s, 1 H), 3.28 (dd, *J* 3 Hz, 10 Hz, 1 H), 4.7–5.0 (complex abs., 3 H). IR (film): 3474 (s), 3070 (m), 1966 (m), 1361 (s) cm^{-1}. Yield 92 %.

4,4,7,7-tetramethyldeca-1,2,8,9-tetraen-5-one (4), was isolated on preparative GLC. ^{1}H NMR (60 MHz, CCl_4): δ 1.06 (s, 6 H), 1.27 (s, 6 H), 3.79 (s, 2 H), 4.6–5.4 (complex abs., 6 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 24.8 (2×CH_3), 25.2 (2×CH_3), 35.0 (C-7), 41.6 (C-4), 71.9 (C-6), 76.8 and 77.6 (C-1 and C-10), 96.9 and 97.3 (C-3 and C-8), 174.0 (C-2 and C-9), 206.7 (C-5). IR (CCl_4): 1955 (s), 1727 (s), 1382 (m) cm^{-1}.

General procedure for the oxidation of 3 *to* 5.[36] The oxidation reagent was added very slowly with vigorous stirring to a solution of *3* (0.21 mol) in 100 ml ether. The reaction was monitored by GLC. Addition of 350 ml (0.23 mol) of the $Na_2Cr_2O_7$ reagent during 3 days was required for complete reaction. The organic phase was separated and the aqueous phase extracted with ether (3×75 ml). The combined extracts were washed with saturated $NaHCO_3$(aq) (75 ml) and water (50 ml). Evaporation of the dried ($MgSO_4$) ether extracts followed by distillation gave *5*.

2,5,5-trimethylocta-1,6,7-trien-4-one (5a), b.p. 63–65 °C/3.5 mmHg. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.23 (s, 6 H), 1.72 (broad s, 3 H), 3.23 (s, 2 H), 4.6–5.3 (complex abs., 5 H). IR (film): 3085 (m), 1957 (s), 1715 (s), 1653 (m), 1370 (m) cm^{-1}. Yield 90 %. 2,4-dinitrophenylhydrazone (recrystallized from ethanol), m.p. 63–64 °C.

2,5,5,8-tetramethylnona-1,6,7-trien-4-one (5b), b.p. 70–72 °C/0.5 mmHg, n_D^{16} 1.4754. ^{1}H NMR (60 MHz, CCl_4): δ 1.17 (s, 6 H), 1.70 (s, 6 H), 1.73 (s, 3 H), 3.14 (s, 2 H), 4.6–5.0 (complex abs., 3 H). IR (film): 3073 (m), 1961 (w), 1702 (s), 1674 (m), 1361 (s) cm^{-1}. Yield 90 %.

2,5,5-trimethyloct-1-en-6-yn-4-one (6), was isolated on preparative GLC (15 % Apiezon L, 180 °C). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.33 (s, 6 H), 1.7–1.9 (complex abs., 6 H), 3.47 (broad s, 2 H), 4.7–5.0 (m, 2 H). IR (film): 3425 (w), 3076 (m), 1717 (s), 1649 (m), 1619 (m), 1377 (s) cm^{-1}.

1,4,4-trimethyl-6-methylenebicyclo[3.2.0]heptan-3-one (7a). A 62 cm long quarts tube, packed with 14 g quarts wool, was heated to 493 °C. The ketone *5a* (5.00 g, 32.4 mmol) was distilled twice through the column at 0.5 mmHg. The product was collected in a trap cooled to −78 °C and the reaction was monitored by the disappearance of the allene absorption in the IR. A complex mixture with two main products of 20 % *8* and 60 % *7a* resulted. Fractional column distillation gave the two main products as a mixture. Analytical amounts were collected on preparative GLC (15 % Apiezon L, 140 °C). On a larger scale *8* was separated from *7a* by adding 41.4 g of a 5 % (w/w) ethanolic (95 %) $AgNO_3$ solution (12.2 mmol $AgNO_3$) to the crude reaction mixture.[17] After *ca.* 4 h, *8* was quantitatively precipitated as the silver acetylide which was filtered off and washed with 95 % ethanol. The ethanolic solution was concentrated at atmospheric pressure and then distilled to give 2.31 g

(46 %) *7a*, 93 %, pure contaminated by two unknown products.

Compound *8* was regenerated by heating 2.86 g (6.5 mmol) of the silver acetylide with 0.75 g (15.3 mmol) NaCN in 5 ml water for 4 h until homogenous solution. Cooling, extraction with ether, drying ($MgSO_4$) and evaporation gave 0.98 g of *8*.

1,4,4-trimethyl-6-methylenebicyclo[3.2.0]heptan-3-one (*7a*), b.p. 69–70 °C/4 mmHg, m.p. −23 to −20 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 3 H), 1.09 (s, 3 H), 1.43 (s, 3 H), 2.28 (d, J 18.29 Hz, 1 H), 2.37 (dq, J 17.42 Hz, 2.40 Hz, 1 H), 2.57 (dd, J 17.42 Hz, 18.29 Hz, 2 H), 2.79 (q, J 2.37 Hz, 2.40 Hz, 1 H), 4.88 (q, J 2.35 Hz, 2.40 Hz, 1 H), 4.92 (q, J 2.37 Hz, 2.40 Hz, 1 H). ^{13}C NMR (100.7 MHz, $CDCl_3$): δ 19.12 (CH_3), 27.12 (CH_3), 27.87 (CH_3), 34.37 (C-1), 43.36 (C-7), 49.26 (C-2), 50.12 (C-4), 61.62 (C-5), 111.45 (CH_2=), 144.64 (C-6), 221.65 (C-3). IR (film): 3085 (w), 1743 (s), 1675 (m), 1382 (m) cm^{-1}. 2,4-dinitrophenylhydrazone (recrystallized from ethanol), m.p. 119–120 °C.

3-ethynyl-2,2,4,4-tetramethylcyclopentanone (*8*), b.p. 69–70 °C/4 mmHg, m.p. 61–62 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.13 (s, 3 H), 1.15 (s, 3 H), 1.17 (s, 3 H), 1.24 (s, 3 H), 2.27 (d, J 2.48 Hz, 1 H), 2.28 (s, 1 H), 2.29 (s, 1 H), 2.70 (d, J 2.48 Hz, 1 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 22.77 (CH_3), 24.39 (CH_3), 27.48 (CH_3), 29.45 (CH_3), 37.06 (C-4), 47.90 (C-2), 51.59 (C-3), 52.02 (C-5), 74.04 (HC≡), 80.60 (−C≡), 220.92 (C-1). IR ($CDCl_3$): 3315 (s), 2125 (w), 1743 (s), 1385 (w), 1375 (m) cm^{-1}.

6-isopropylidene-1,4,4-trimethylbicyclo[3.2.0]heptan-3-one (*7b*). Distillation of 5.00 g (26.0 mmol) *5b* twice through the tube described under *7a*, kept at 490 °C/0.7 mmHg, gave a complex mixture including *7b* (69 %). Fractional column distillation yielded 2.55 g (51 %) *7b*, b.p. 68 °C/0.2 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.02 (s, 3 H), 1.09 (s, 3 H), 1.39 (s, 3 H), 1.49 (d, J 1.40 Hz, 3 H), 1.54 (d, J 0.87 Hz, 3 H), 2.25 (d, J 17.57 Hz, 2 H), 2.39 (broad d, J 17.3 Hz, 1 H), 2.53 (d, J 17.57 Hz, 1 H), 2.77 (broad s, 1 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 18.67 (CH_3), 19.58 (CH_3), 19.85 (CH_3), 26.59 (CH_3), 28.82 (CH_3), 33.51 (C-1), 40.92 (C-7), 49.20 (C-2), 50.62 (C-4), 60.30 (C-5), 126.97 and 127.89 (C-6 and C=), 222.42 (C-3). IR (film): 1735 (s), 1449 (s), 1376 (s) cm^{-1}.

General procedure for the preparation of 11. A solution of *7* (18 mmol) in 40 ml dry CH_2Cl_2 was kept at room temperature in a water bath. A mixture of m-chloroperbenzoic acid (38 mmol) and $NaHCO_3$ (46 mmol) was added portionwise to the stirred solution. The reaction mixture was stirred vigorously overnight and then 10 % $Na_2S_2O_3$ (aq., 35 ml) was added dropwise. Stirring for another 0.5 h, separation of the organic layer, extraction of the water phase with CH_2Cl_2 (2×20 ml), washing of the collected organic phases with saturated $NaHCO_3$ (aq) (20 ml) and brine (20 ml), drying ($MgSO_4$) and evaporation gave crude *11* which was found pure enough for the next reaction.

5,5,9-trimethyl-2,6-dioxa-7-oxobicyclo[4.3.0]octylspiro[2.7]decane (11a). GLC-analysis (capillary wall-coated SP2100, 25 m) revealed the formation of two products in the ratio of 88:12, probably the two epoxides (*exo* and *endo* respectively). MS: 196 (M^+). ^{1}H NMR (98 MHz, $CDCl_3$): δ 1.27 (s, 3 H), 1.40 (s, 3 H), 1.45 (s, 3 H), 2.15 (d, J 13 Hz, 1 H), 2.36 (d, J 13 Hz, 1 H), 2.56–2.81 (m, 4 H), 3.24 (d, J 4 Hz, 1 H). For the minor isomer all proton resonances were indistinguishable from the major one except δ 3.62 (d, J 3 Hz, 1 H). IR ($CDCl_3$): 1718 (s), 1289 (m), 1243 (m) cm^{-1}. The crude yield was 100 %.

3,3,5,5,9-pentamethyl-2,6-dioxa-7-oxobicyclo[4.2.0]octylspiro[2.7]decane (11b). GLC-analysis (capillary, wall-coated SP2100, 25 m) revealed two products in the ratio of 95:5 probably the *exo*- and *enso*-epoxides respectively. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.17 (s, 3 H), 1.38 (s, 3 H), 1.43 (s, 3 H), 1.45 (s, 3 H), 1.47 (s, 3 H), 1.6–2.4 (complex abs., 3 H), 2.55 (s, 2 H). The crude yield was 100 %.

1,5,5-trimethyl-4-oxabicyclo[4.2.0]octan-3,7-dione (*12*). *From* 11a. To a solution of 3.54 g (18.0 mmol) *11a* dissolved in 30 ml dry ether kept at room temperature with a water bath, was added 4.10 g (18.0 mmol) H_5IO_6 with stirring. GLC-analysis of aliquots treated with saturated $NaHCO_3$ (aq), revealed that the minor component of the epoxide mixture reacted fast (ca. $\frac{1}{2}$ h for reaction) while the major one needed 20 h for complete reaction. Only one product was formed. Enough water (5 ml) to dissolve the precipitated HIO_3 was added, the ether layer separated and the water phase extracted with ether (4×15 ml). The collected ether phases were extracted with saturated Na_2CO_3 (aq) (1×10 ml) and brine (1×10 ml), dried ($MgSO_4$) and evaporated to give 3.28 g (100 %) *12* as a yellow oil, which crystallized upon standing. Recrystallization from ether or *t*-butyl methyl ether gave an analytically pure sample.

From 11b. Following the preceding procedure 3.30 g (18.0 mmol) *11b* and 4.10 g (18.0 mmol) H_5IO_6 in 30 ml dry ether yielded three products *12, 13* and *14* in a ratio of 75:14:11, respectively. *12* was recrystallized from ether or *t*-butyl methyl ether. The mother liquor was concentrated and ether/pentane (1:1) was added. After five days at −10 °C *13* crystallized and was recrystallized from ether. The concentrated mother liquor was dissolved in a small amount of ethanol and titrated with a 0.25 M 2,4-dinitrophenylhydrazine solution. The selective reaction of *12* and *13* was monitored by GLC. The solution was filtered and concentrated. The residue was dissolved in $CHCl_3$ and washed with 4 M HCl (aq), saturated $NaHCO_3$ (aq) and water, dried ($CaCl_2$) and evaporated. The residue was chromatographed on silica, and elution with $CHCl_3$ afforded *14* as a liquid. *12*: m.p. 99−100 °C. MS: 182 (M^+). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.43 (s, 3 H), 1.55 (s, 3 H), 1.57 (s, 3 H), 2.80 (s, 1 H), 2.81 (s, 1 H), 2.90 (d, *J* 4.2 Hz, 1 H), 2.91 (d, *J* 4.4 Hz, 1 H), 3.03 (dd, *J* 4.2 Hz, 4.4 Hz, 1 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 26.70 (2×CH_3), 28.07 (CH_3), 29.49 (C-1), 40.08 (C-2), 57.95 (C-8), 69.60 (C-6), 80.56 (C-5), 170.10 (C-3), 205.25 (C-7). The IR spectrum was in accordance with lit.[8]

13. m.p. 131−132 °C. MS (IP 70 eV): *m/z* 224.1412 (M^+), calc. for $C_{13}H_{20}O_3$ 224.1412. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.18 (s, 3 H), 1.28 (s, 3 H), 1.34 (s, 3 H), 1.59 (s, 3 H), 1.60 (s, 3 H), 1.94 (s, 1 H), 2.32 (d, *J* 17.8 Hz, 1 H), 2.69 (s, 2 H), 2.69 (d, *J* 17.8 Hz, 1 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 22.99 (CH_3), 27.06 (CH_3), 27.16 (CH_3), 31.07 (CH_3), 33.93 (CH_3), 34.45 (C-1), 42.71 (C-2), 49.37 (C-7), 51.70 (C-9), 59.68 (C-6), 83.08 (C-5), 171.19 (C-3), 217.54 (C-8). IR (KBr): 1735 (s), 1715 (s), 1395 (s), 1387 (s), 1327 (m) cm^{-1}.

14. MS: 224 (M^+). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.04 (s, 3 H), 1.11 (s, 3 H, 1.27 (s, 3 H), 1.30 (s, 3 H), 1.54 (s, 3 H), 1.84 (d, *J* 14.02 Hz, 1 H), 1.92 (d, *J* 14.02 Hz, 1 H), 2.33 (s, 1 H), 2.54 (s, 2 H). ^{13}C NMR (15.0 MHz, $CDCl_3$): δ 25.5 (CH_3), 25.9 (CH_3), 27.6 (CH_3), 31.5 (CH_3), 32.9 (CH_3), 36.5 (C-1), 43.1 (C-2), 46.7 (C-8), 52.2 (C-9), 62.0 (C-6), 81.5 (C-5), 171.1 (C-3), 220.9 (C-7). IR ($CDCl_3$): 1730 (s) cm^{-1}.

1,5,5,7,7-pentamethyl-4-oxabicyclo[4.3.0]nona-3,8-dione (13). To 1.60 g (7.1 mmol) *11b* was added 20 ml 88 % (w/w) aqueous HCO_2H. the mixture was stirred at room temperature until the reaction was completed. The main components of the complex product were *13* (45 %) and *14* (30 %). Evaporation resulted in a viscous oil which by trituration with ether gave 0.61 g (38 %) of crystalline *13*.

3,3,7-trimethyl-2,9-dioxatricyclo[3.3.1.0^{4,7}]nonane (lineatin) (1). *Reduction with DIBAH*. This is a modification of published procedures.[4,6] A suspension of 3.20 g (17.6 mmol) finely powdered *12* in 70 ml abs. ether was cooled to −60−70 °C and 39 ml (1.0 M in hexane, 39 mmol) DIBAH was added dropwise with stirring. The mixture was stirred for 2 h when 64 ml saturated NH_4Cl (aq) was added dropwise. When the addition was complete, the mixture was heated to 0 °C, acidified with 4 M HCl (aq) (46 ml) and stirred for another 1.5 h. The ether layer was separated and the water phase extracted with ether (4×60 ml). The collected extracts were washed with saturated $NaHCO_3$ (aq) (1×60 ml) and dried ($MgSO_4$). The solution was concentrated by carefully lowering the pressure to 10 mmHg and keeping the bath temperature below 35 °C. Distillation (b.p. 60−62 °C/3 mmHg) yielded 2.17 g (74 %) *1*. The spectral data were in accordance with those in the lit.[6]

Reduction with LiAl(OBu^t)$_3$H. To a solution of 9.79 g (53.7 mmol) *12* in 700 ml abs. ether was added 27.90 g (109.7 mmol) $LiAl(OBu^t)_3H$ portionwise during 1 h. The suspension was stirred for 20 h when it was acidified with 4 M HCl (aq) (75 ml). The ether layer was decanted and the thick suspension was washed with ether (4×75 ml). The collected extracts were washed with saturated $NaHCO_3$ (100 ml) and dried ($MgSO_4$). Concentration as described above and distillation yielded 6.7 g (74 %) *1*.

Dichloroketene addition to 2,5,5-trimethylcyclopentadiene (15). To a refluxing mixture of 2.90 g (26.8 mmol) *15* and 5.60 g (38.0 mmol) $Cl_2CHCOCl$ in 25 ml dry pentane, 4.30 g (42.5 mmol) Et_3N in 25 ml dry pentane was added dropwise. The solution was refluxed with stirring for 18 h, cooled and water added. The organic layer was separated and the aqueous phase extracted several times with pentane. The combined extracts were washed with dilute HCl (aq), 5 % $NaHCO_3$, dried (Na_2SO_4) and evaporated. Distillation gave 1.50 g (26 %) *16* and *17*, b.p. 64−65 °C/1.0 mmHg, as an unseparable mixture. The ratio between *16* and *17* was found by GLC- and ^{1}H NMR-analysis to be 52:48.

The mixture of *16* and *17* was reduced with Zn/HOAc[37] to a mixture of either *18a* and *19a* or *18b* and *19b*. The components could be separated on preparative GLC (15 % SE52, 120 °C).

7,7-dichloro-1,4,4-trimethylbicyclo[3.2.0]hept-2-en-6-one (16), ^{1}H NMR (98 MHz, CCl_4): δ 1.11 (s, 3 H), 1.25 (s, 3 H), 1.60 (s, 3 H), 3.26 (d, *J* 1.0 Hz, 1 H), 5.55 (dd, *J* 1.0 Hz, 5.0 Hz, 1 H), 5.72 (d, *J* 5.0 Hz, 1 H). IR (film): 1805 (s) cm^{-1}.

7,7-dichloro-2,4,4-trimethylbicyclo[3.2.0]hept-2-en-6-one (17), ^{1}H NMR (98 MHz, CCl_4): δ 1.07 (s, 3 H), 1.19 (s, 3 H), 1.92 (broad s, 1 H), 3.72 (d, *J* 7.5 Hz, 1 H), 3.85 (dm, *J* 7.5 Hz, 1 H), 5.44 (quintet, *J* 1.5 Hz, 1 H). IR (film): 1805 (s) cm^{-1}.

1,4,4-trimethylbicyclo[3.2.0]hept-2-en-6-one (18a). Anal. $C_{10}H_{14}O$:C, H. ^{1}H NMR (98 MHz, CCl_4): δ 1.06 (s, 3 H), 1.15 (s, 3 H), 1.51 (s, 3 H), 2.80 (s, 2 H), 2.86 (s, 1 H), 5.49 (d, *J* 5.5 Hz, 1 H), 5.55 (d, *J* 5.5 Hz, 1 H). IR (CCl_4): 3090 (w), 1790 (s) cm^{-1}.

2,4,4-trimethylbicyclo[3.2.0]hept-2-en-6-one (19a). Anal. $C_{10}H_{14}O$:C, H. ^{1}H NMR (98 MHz, CCl_4): δ 0.99 (s, 3 H), 1.12 (s, 3 H), 1.71 (d, *J* 1.5 Hz, 3 H), 2.5–3.4 (complex abs., 4 H), 5.20 (d, *J* 1.5 Hz, 1 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 14.4 (CH_3), 24.8 (CH_3), 30.7 (CH_3), 39.5 (C-5), 47.2 (C-4), 52.2 (C-7), 73.0 (C-1), 137.7 (C-3), 137.9 (C-2), 206.2 (C-6). IR (CCl_4): 3050 (w), 1785 (s) cm^{-1}.

endo-*7-chloro-1,4,4-trimethylbicyclo[3.2.0]hept-2-en-6-one* (18b). Anal. $C_{10}H_{13}ClO$: C, H. ^{1}H NMR (98 MHz, CCl_4): δ 1.10 (s, 3 H), 1.24 (s, 3 H), 1.61 (s, 3 H), 2.93 (d, *J* 2.8 Hz, 1 H), 4.54 (d, *J* 2.8 Hz, 1 H), 5.51 (d, *J* 5.3 Hz, 1 H), 5.65 (d, *J* 5.3 Hz, 1 H). IR (CCl_4): 3090 (w), 1800 (s) cm^{-1}.

endo-*7-chloro-2,4,4-trimethylbicyclo[3.2.0]hept-2-en-6-one* (19b). ^{1}H NMR (60 MHz, CCl_4): δ 1.02 (s, 3 H), 1.18 (s, 3 H), 1.88 (d, *J* 1 Hz, 3 H), 3.30 (dd, *J* 3 Hz, 7 Hz, 1 H), 3.73 (broad, t, *J* 7 Hz, 1 H), 4.87 (dd, *J* 3 Hz, 8.5 Hz, 1 H), 5.38 (broad s, 1 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 16.4 (CH_3), 24.1 (CH_3), 30.8 (CH_3), 47.8 (CH), 48.9 (C-4), 63.8 (CH), 68.7 (CH), 134.6 (C-2), 140.5 (C-3), 199.8 (C-6). IR (CCl_4): 3050 (w), 1795 (s) cm^{-1}.

Dichloroketene addition to 2,4,4-trimethyl-6-methoxy-2H-pyran (21). *By the method of Krepski and Hassner.*[28] To a stirred mixture of 3.28 g (21.0 mmol) *21* and 1.50 g (23.0 mmol) activated Zn in 50 ml dry ether, kept at room temperature , was added a solution of 2.40 ml (3.88 g, 21.3 mmol) Cl_3CCOCl and 2.00 ml (3.26 g, 21.2 mmol) $POCl_3$ in 40 ml dry ether over a period of 1 h. The mixture was heated under reflux for 4 h, cooled and filtered through Celite which subsequently was washed with 50 ml ether. The etheral solution was concentrated under vacuum to ca. 15 ml and an equal volume of pentane added. The solution was decanted from the precipitated zink salts and washed successively with water, cold saturated $NaHCO_3$ (aq), brine and dried (Na_2SO_4). Evaporation and distillation gave 2.21 g (45 %) *22*, b.p. 54–56 °C/0.08 mmHg.

By the method of Bak and Brady.[27] To a stirred, refluxing mixture of 1.96 g (12.5 mmol) *21* and 2.80 g (42.8 mmol) activated Zn in 250 ml dry ether was added dropwise 1.41 ml (2.28 g, 12.5 mmol) Cl_3CCOCl in 250 ml dry ether during 5 h. The mixture was stirred at reflux for an additional 6 h. The excess zink was filtered and washed with ether. The solution was concentrated to about 50 ml and an equal amount of pentane was added. The organic phase was decanted from the precipitated zink salts, evaporated and distilled to yield 0.17 g (6 %) of *22*.

8,8-dichloro-3,3,5-trimethyl-5-oxabicyclo[4.2.0]oct-4-en-7-one (22), b.p. 54–56 °C/0.08 mmHg, MS: 238,236,234 (M^+). ^{1}H NMR (98 MHz, CCl_4): δ 1.28 (s, 3 H), 1.82 (dd, *J* 1.4 Hz, 2.3 Hz, 3 H), 3.90 (dm, *J* 5.5 Hz, 1 H), 4.53 (d, *J* 5.5 Hz, 1 H), 5.52 (m, 1 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 21.2 (CH_3), 25.7 (CH_3), 28.8 (CH_3), 56.7 (C-6), 70.8 (C-1), 73.1 (C-3 and C-8), 123.7 (C-5), 129.8 (C-4), 189.4 (C-7). IR (film): 2985 (m), 2965 (m), 1805 (s), 1390 (m), 1365 (m), 1130 (s), 1005 (m), 940 m), 765 (s) cm^{-1}.

3,3,5-trimethyl-2-oxabicyclo[4.2.0]oct-4-en-7-one (23). To a stirred, refluxing solution of 1.00 g (4.25 mmol) *22* and 21 mg (0.13 mmol) azobisisobutyronitrile in 5 ml dry cyclohexane was added 4.95 g (17.0 mmol) Bu_3SnH in 5 ml dry cyclohexane dropwise during 30 min. The mixture was refluxed for an additional 2 h. The cyclohexane was distilled at atmospheric pressure. Distillation gave 0.72 g (100 %) *23*, b.p. 97–100 °C/8 mmHg, together with a small amount of unreacted Bu_3SnH. An analytical sample was obtained by preparative GLC (10 % Apiezon L, 150 °C). ^{1}H NMR (98 MHz, C_6D_6): δ 1.06 (s, CH_3), 1.15 (s, 3 H), 1.70 (dd, *J* 1.0 Hz, 1.5 Hz, 3 H), 2.7–2.9 (complex abs., 3 H), 4.15 (octet, *J* 2.5 Hz, 2.5 Hz, 3.5 Hz, 1 H), 5.2–5.3 (broad q, *J* 2.5 Hz, 1.5 Hz, 1 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 21.2 (CH_3), 25.6 (CH_3), 29.3 (CH_3), 52.5 (C-6), 59.2 (C-1), 61.7 (C-8), 71.5 (C-3), 122.5 (C-5), 129.2 (C-4), 201.5 (C-7). IR (CCl_4): 1795 (s), 1390 (m), 1365 (m), 1125 (m) cm^{-1}.

Photochemical additions

Addition of ketene dimethylacetal to 2,4,4-trimethyl-2-cyclopentenone (26). A solution of 2.70 g (21.7 mmol) *26* and 25.6 g (291 mmoles) ketene dimethylacetal in 120 ml dry pentane was cooled to 0 °C (ice/water) and irradiated for 19 h, monitoring the reaction by GLC. Evaporation and distillation (b.p. 68–72 °C/0.15 mmHg) gave 3.36 g (73 %) of *27a* and *28a* as a 71:29 mixture as shown by GLC. Separation by preparative GLC (15 % PEG 4000, 160 °C), gave analytical samples.

*6,6-dimethoxy-1,4,4-trimethylbicyclo[3.2.0]heptan-2-one (*27a*).* MS (IP 70 eV): 212 (M^+). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.94 (broad s, 3 H), 1.30 (s, 3 H), 1.32 (s, 3 H), 1.92 (broad d, J 12.8 Hz, 1 H), 1.98 (broad d, J 17.3 Hz, 1 H), 2.28 (s, 1 H), 2.31 (broad d, J 12.8 Hz, 1 H), 2.89 (d, J 17.3 Hz, 1 H), 3.09 (s, 3 H), 3.19 (s, 3 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 21.96 (CH_3), 24.68 (CH_3), 30.48 (CH_3), 36.43 (C-4), 41.65 (C-7), 47.66 (CH_3O), 48.18 (CH_3O), 51.57 (C-3), 61.80 (C-5), 101.13 (C-6), 222.60 (C-2). The resonance of C-1 is probably obscured by another resonance. IR (CCl_4): 1740 (s) cm^{-1}.

*7,7-dimethoxy-1,4,4-trimethylbicyclo[3.2.0]heptan-2-one (*28b*).* MS (IP 70 eV): 212 (M^+). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.94 (s, 3 H), 1.07 (s, 3 H), 1.28 (s, 3 H), 1.9–2.1 (complex abs., 3 H), 2.40 (dd, J 13.3 Hz, 9.4 Hz, 1 H), 2.68 (d, J 16.9 Hz, 1 H), 3.13 (s, 3 H), 3.19 (s, 3 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 16.64 (CH_3), 23.49 (CH_3), 29.08 (CH_3), 31.15 (C-6), 36.22 (C-4), 45.48 (CH_3O), 48.60 (C-5), 49.64 (CH_3O), 51.18 (C-3), 61.95 (C-1), 98.30 (C-7), 218.48 (C-2). IR (CCl_4): 1740 (s) cm^{-1}.

Hydrolysis of 27a *and* 28a. the mixture (329 mg) was suspended in 20 ml water and 6 drops conc. HCl (aq) was added with vigorous stirring. After 14 h at room temperature the mixture was neutralized with saturated Na_2CO_3 (aq), extracted with ether (3×20 ml), dried ($MgSO_4$) and evaporated to yield 180 mg of *29* and *30a* as a 72:28 mixture. The two compounds were separated by preparative GLC (20 % SP2100, 160 °C), *31a* as a mixture of stereoisomers.

*1,4,4-trimethylbicyclo[3.2.0]heptan-2,6-dione (*29*).* MS: 166 (M^+). ^{1}H NMR (60 MHz, CCl_4): δ 0.97 (s, 3 H), 1.22 (s, 3 H), 1.45 (s, H), 2.12 (d, J 16 Hz, 1 H), 2.48 (d, J 16 Hz, 1 H), 2.93 (s, 2 H), 2.98 (s, 1 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 19.3 (CH_3), 24.2 (CH_3), 28.8 (CH_3), 36.0 (C-4), 42.4 (C-1), 50.3 (C-3), 56.7 (C-7), 77.2 (C-5), 203.3 (C-6), 213.4 (C-2). IR (CCl_4): 1790 (s), 1745 (s) cm^{-1}.

*Methyl (2,5,5-trimethyl-3-oxocyclopentanyl)acetate (*30a*).* MS: 198 (M^+). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.93 (s, 3 H), 1.07 (d, J 6.75 Hz, 3 H), 1.15 (s, 3 H), 2.0–2.6 (complex abs., 6 H), 3.70 (s, 3 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 13.76 (CH_3), 22.24 (CH_3), 27.57 (CH_3), 34.09 (C), 48.14 (CH_3O), 50.40 (CH), 51.74 (CH), 53.79 (CH_2), 59.89 (CH_2), 173.52 (O–C=O), 217.62 (C=O). IR ($CDCl_3$): 1734 (s) cm^{-1}.

Addition of ketene diethylacetal to 26. Following the same procedure as for the dimethylacetal, a solution of 2.68 g (21.6 mmol) *26* and 35.5 g (306 mmol) ketene diethylacetal in 140 ml dry pentane was cooled to −78 °C (dry ice/methanol) and irradiated for 11 h, monitoring the reaction on GLC. Evaporation and distillation yielded 3.01 g (58 %) of *6,6-diethoxy-1,4,4-trimethylbicyclo[3.2.0]heptan-2-one (*27b*)* and *7,7-diethoxy-1,4,4-trimethylbicyclo[3.2.0]heptan-2-one (*28b*),* b.p. 66–67 °C/0.12 mmHg, as a 67:33 mixture as shown by GLC. ^{1}H NMR (60 MHz, CCl_4): δ 0.90 (s, 3 H), 1.03 (s, 3 H), 1.17 (s, 3 H), 1.20 (s, 3 H), 1.23 (s, 3 H), 1.30 (s, 3 H), 0.8–1.4 (complex abs., 12 H), 1.6–3.0 (complex abs., 10 H), 3.1–3.6 (complex abs., 8 H). IR (CCl_4): 1735 (s) cm^{-1}.

27b, MS (IP 70 eV): 240 (M^+). ^{13}C NMR (15.0 MHz, CCl_4): δ 15.1 (2×CH_3), 22.0 (CH_3), 24.8 (CH_3), 30.4 (CH_3), 36.1 (C-4), 42.0 (C-7), 50.9 (C-3), 55.5 (2×CH_2), 62.0 (C-5), 100.2 (C-6), 218.2 (C-2). The resonance of C-1 was probably obscured by another resonance.

28b, MS (IP 70 eV): 240 (M^+). ^{13}C NMR (15.0 MHz, CCl_4): δ 15.0 (CH_3), 16.6 (CH_3), 23.5 (CH_3), 28.9 (CH_3), 31.4 (CH_3), 35.8 (C-4), 42.4 (C-6), 45.5 (CH_2), 50.6 (CH_2), 51.0 (CH_2), 61.7 (C-5), 97.1 (C-7), 214.9 (C-2). The resonance of C-1 was probably obscured by another resonance.

Hydrolysis of 27b *and* 28b. Following the same procedure as for *27a* and *28a,* the mixture (337 mg) gave 216 mg of *29* and *30b* as a 67:33 mixture. Separation by preparative GLC (10 % PEG 4000, 160 °C) gave analytical samples.

*Ethyl (2,5,5-trimethyl-3-oxocyclopentanyl)acetate (*30b*).* MS: 212 (M^+). ^{1}H NMR (200

MHz, $CDCl_3$): δ 0.93 (s, 3 H), 1.07 (d, J 6.7 Hz, 3 H), 1.16 (s, 3 H), 1.27 (t, J 7.1 Hz, 3 H), 2.0–2.6 (complex abs., 6 H, 4.16 (q, J 7.1 Hz, 2 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 13.7 (CH_3), 14.2 (CH_3), 22.2 (CH_3), 27.6 (CH_3), 34.0 (CH_2), 36.5 (C), 47.7 (CH), 50.1 (CH), 53.2 (CH_2), 59.7 (CH_2), 171.3 (O–C=O), 214.1 (C=O). IR (CCl_4): 1745 (s) cm^{-1}. The minor isomer was obscured by the major one in both the ^1H and ^{13}C NMR spectra.

Addition of ketene diethylacetal to 3-methyl-2-cyclopentenone (31). A solution of 1.70 g (17.7 mmol) *31* and 29.5 g (250 mmol) ketene diethylacetal in 250 ml dry pentane was cooled to −78 °C (dry ice/methanol) and irradiated for 11 h. Evaporation and distillation afforded 2.01 g (53 %) *6,6-diethoxy-5-methylbicyclo-[3.2.0]heptan-2-one (32)*, b.p. 72–74 °C/0.15 mmHg, n_D^{19} 1.4593, MS (IP 70 eV): 212 (M^+). ^1H NMR (60 MHz, CCl_4): δ 1.08 (d, J 6.5 Hz, 3 H), 1.10 (d, J 6.5 Hz, 3 H), 1.25 (s, 3 H), 1.4–2.7 (complex abs., 7 H), 3.40 (q, J 6.5 Hz, 2 H), 3.42 (q, J 6.5 Hz, 2 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 14.9 (CH_3), 15.1 (CH_3), 20.7 (CH_3), 28.4 (C-4), 33.3 (C-7), 38.2 (C-3), 43.8 (C-1), 52.5 (C-5), 56.7 (2×CH_2), 101.2 (C-6), 216.3 (C-2). IR (CCl_4): 1740 (s) cm^{-1}.

5-methylbicyclo[3.2.0]heptan-2,6-dione (33). Following the same procedure as for *27* and *28,* 202 mg (0.95 mmol) *32* yielded 125 mg (95 %) *33*. ^1H NMR (200 MHz, $CDCl_3$): δ 1.38 (s, 3 H), 1.7–1.9 (m, 1 H), 2.3–2.7 (complex abs., 4 H), 2.98 (dd, J 5.4, 1.91 Hz, 1 H), 3.55 (dd, J 10.6, 19.1 Hz, 1 H). ^{13}C NMR (15.0 MHz, CCl_4): δ 18.8 (CH_3), 29.6 (CH_2), 36.7 (CH_2), 42.6 (CH), 49.2 (CH_2), 68.3 (C), 207.5 (C=O), 213.2 (C=O). IR (CCl_4): 1789 (s), 1744 (s) cm^{-1}.

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