Synthesis and Properties of 2,4,6-Trimethylenetricyclo[3.3.0.0^{3,7}]octane (Stellatriene) and Its Alkyl Derivatives. Candidates for a Two-Step Cope Rearrangement

Rolf Gleiter* and Christoph Sigwart

*Organisch Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270,
D-69120 Heidelberg, Germany*

The synthesis of 2,4,6-trimethylenetricyclo[3.3.0.0^{3,7}]octane (stellatriene, **9**), its hexamethyl derivative **37**, and the spirocyclic derivatives **67** and **68**, substituted at the carbon atom of the saturated bridge of the tricyclic system, are described. Key steps in the syntheses include an intramolecular Paterno–Büchi reaction leading to tetracyclic oxetanes (e.g., **22b**, **39**, **47**, **59**, and **60**) as well as the cleavage of the oxetane ring induced by various bases. During the synthesis several dienones were prepared (**35**, **41**, **50**, **63**, and **64**). The trienes and the dienones rearrange to triquinane derivatives at temperatures between 25 and 50 °C. The half-lives of the molecules in solution have been determined, which indicate only a moderate effect of the methyl groups on the stability. The rearranged products can best be explained by assuming a stepwise Cope rearrangement via two allylic fragments.

Some time ago we postulated a strong through-bond interaction of two perpendicular π-systems spanning the 1,3- and 2,4-positions of a four-membered ring, such as **1**.[1]


Our prediction was substantiated by investigating the UV and PE spectra of **2**.[2] It was found that both π-fragments interact considerably. This in turn initiated the question of whether a similar interaction can be detected if one replaces the central four-membered ring in **1** by another unit such as a six- to eight-membered ring (**3–5**). For **3** and **4** this means that the two π-fragments are held not any more perpendicularly. Investigations of the PE spectra of **6–8** show a considerable splitting of the π-bands from 1.2 (**6**) to 0.7 eV (**8**).[3] Our synthesis of **7**, **8**, and related
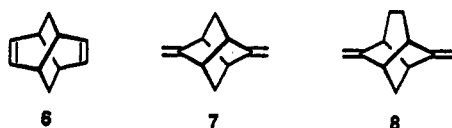

species allowed us to begin to think about introducing additional double bonds into the molecule, which automatically leads to systems such as **9–12**. In these cases not only the possible interactions but also the beauty of the molecules[5] initiated our studies.

In this paper we would like to present our investigations on 2,4,6-trimethylenetricyclo[3.3.0.0^{3,7}]octane (**9**) (stellatriene) and alkyl-substituted products. During our efforts
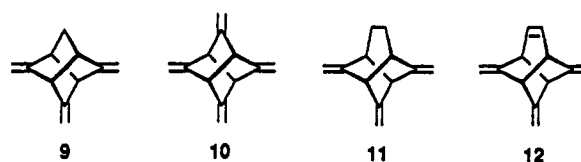
to synthesize **9**[6] we realized that stellatriene rearranges easily to the triquinane derivative **13**.

Scheme 1[a]
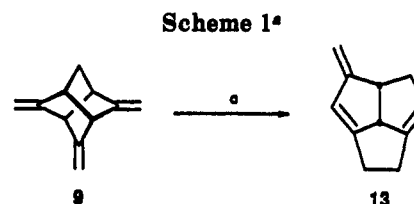

[a] Key: (a) 25 °C.

Synthesis of Tricyclo[3.3.0.0^{3,7}]octane Derivatives with Three Exocyclic Double Bonds. Strategy. We presumed that steric effects might stabilize **9** by raising the activation energy of the rearrangement **9** to **13**. Sterically more demanding substituents can be introduced at the olefinic methylene carbon atoms and/or at the saturated methylene carbon atom (C(8)). In view of our spectroscopic investigations and for reasons of product analysis we were also interested in maintaining C_2 symmetry in the substituted derivatives. Because of these considerations we developed the retrosynthetic approach to the alkyl-substituted trienes that is presented in Scheme 2.

If we disconnect along bond A we require the bicyclo[2.2.1]heptene derivative **15**, having an exocyclic double bond at C(3). Further retro analysis leads to a 5,5-disubstituted cyclopentadiene derivative **16** and the allenyl ketone **17**. Disconnection of bond B leads to the bicyclo[2.2.1]heptene derivative **18** which contains an exocyclic double bond at C(7). This compound should be

* Abstract published in *Advance ACS Abstracts*, January 15, 1994.

(1) Bischof, P.; Gleiter, R.; Haider, R. *J. Am. Chem. Soc.* 1978, *100*, 1036.

(2) Gleiter, R.; Toyota, A.; Bischof, P.; Krennrich, G.; Dressel, J.; Pansegrau, P. D.; Paquette, L. A. *J. Am. Chem. Soc.* 1988, *110*, 5490.

(3) Gleiter, R.; Kissler, B.; Ganter, C. *Angew. Chem.* 1987, *99*, 1292. *Angew Chem., Int. Ed. Engl.* 1987, *26*, 1252.

(4) Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* 1990, *23*, 369 and references cited therein.

(5) Hofmann, R.; *J. Aestetics Art Criticism* 1990, *48*, 191.

(6) (a) Gleiter, R.; Sigwart, C.; Kissler, B. *Angew. Chem.* 1989, *101*, 1561. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 1525. (b) Smith, A. B.; Dieter, R. K. *Tetrahedron Lett.* 1976, 327.

Scheme 2. Retrosynthetic Approach to 14
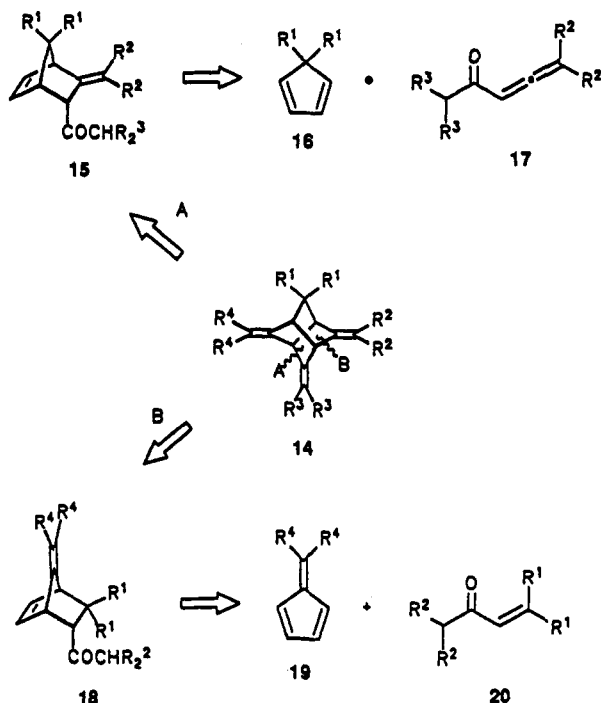
Scheme 3. Key Reactions To Achieve the Tricyclo[3.3.0.0³,⁷]octane System
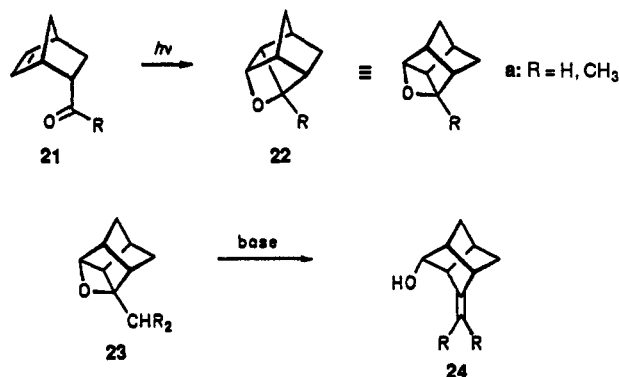
available by a Diels–Alder reaction of a 6,6-disubstituted fulvene **19** and an α,β-unsaturated ketone **20**.

Key Reactions. As we will see later there are two key steps in the synthesis of stellatrienes, the first one being the intramolecular Paterno–Büchi reaction of 5-*endo*-acyl-substituted norbornene derivatives such as **21**. This reaction has been introduced by Sauers et al.,[7,8] and its regiospecificity guarantees the synthesis of the desired tricyclic carbon skeleton. The work by Sauers et al.[7,8] and Nakazaki et al.[9,10] has shown that the intramolecular Paterno-Büchi reaction can be applied fruitfully to a variety of bicyclic systems. The second key step is the cleavage of the oxetane ring which has been carried out by reduction with LiAlH₄ or by bases.[7-11] The latter

variant can be used if at least one of the α-C-atoms is alkyl substituted and if this substituent bears at least one β-H-atom. We prefer this base-induced cleavage, since this method allows the introduction of an exocylic double bond together with the functionalization of the adjacent carbon bridge. However, we have found in the course of our investigations that the successful cleavage of the oxetane ring depends in a subtle manner on the tetracyclic molecule; hence, the most efficient reagents for this step have to be found for each system individually.

Starting Materials. Starting materials for our approach are the known dienophiles **25–27** and the dienes **28** and **29**. The synthesis of acetylallene (**25**) has been
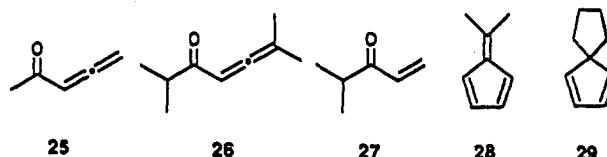
described by Buono.[12] For the synthesis of **26** an analogous approach[13,14] has been used starting from 2,6-dimethyl-heptane-3,5-dione.[15] The preparation of isopropyl vinyl ketone (**27**) has been carried out analogously to that of ethyl vinyl ketone as suggested by McMahon.[16] To obtain 6,6-dimethylfulvene (**28**) we used the procedure suggested by Little and Stone.[17] The spiro compound **29** was prepared according to the method of Wilcox and Craig[18] in a straightforward way from cyclopentadiene and 1,4-dibromobutane. We preferred the spiro compound instead of the 5,5-dialkyl-1,3-cyclopentadiene in order to avoid complications that might occur from alkyl migration.

Synthesis of 2,4,6-Trimethylenetricyclo[3.3.0.0³,⁷]-octane (Stellatriene). The synthesis of stellatriene (**9**) has been described in a preliminary communication;[6] therefore, we will only briefly review the steps (Scheme 4).

For the synthesis of the norbornene derivative **33**, which represents the key compound of the reaction sequence, we used two routes. The first starts with the *endo*-adduct of cyclopentadiene and maleic anhydride (**30**). This product can be converted to the aldehyde **31** in four steps by known procedures.[19] In two further steps the key compound *endo*-2-acetyl-3-methylenebicyclo[2.2.1]hept-5-ene (**33**) is made available.[6a] This compound can be obtained more efficiently and more economically from the cycloaddition of acetylallene (**25**) and cyclopentadiene.[6a] Irradiation of **33** in ether then yields the oxetane **22b** via an intramolecular Paterno–Büchi reaction.[6] By treatment of **22b** with lithium diisopropylamide (LDA) the alcohol **34** was available in 81% yield. Subsequent oxidation leads to 4,6-dimethylenetricyclo[3.3.0.0³,⁷]octan-2-one (**35**), which can be transformed to **9** via a Wittig
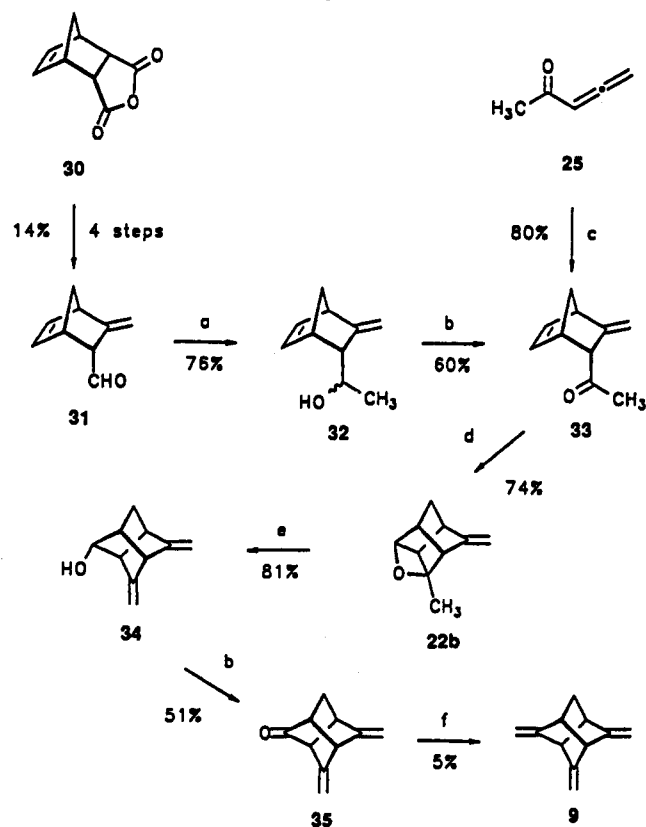
(7) Sauers, R. R.; Schinski, W.; Mason, M. M. *Tetrahedron Lett.* 1969, 79. Sauers, R. R.; Whittle, J. A. *J. Org. Chem.* 1969, *34*, 3579.

(8) Sauers, R. R.; Rousseau, A. D. *J. Am. Chem. Soc.* 1972, *94*, 1776. Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* 1974, *39*, 1850. Sauers, R. R.; Lynch, D. C. *J. Org. Chem.* 1980, *45*, 1286.

(9) Nakazaki, M.; Naemura, K.; Kondo, Y. *J. Org. Chem.* 1976, *41*, 1229. Review: Naemura, K. In *Carbocyclic Cage Compounds*; Osawa, E., Yonemitsu, O., Eds.; Verlag Chemie; Weinheim, 1992; p 61.

(10) Nakazaki, M.; Naemura, K.; Harita, S. *Bull. Chem. Soc. Jpn.* 1975, *48*, 1907.

(11) Gleiter, R.; Kissler, B. *Tetrahedron Lett.* 1987, *28*, 6151.

(12) Buono, G. *Synthesis* 1981, 872.

(13) Sugita, T.; Eida, M.; Ito, H.; Komatsu, N.; Abe, K.; Suama, M. *J. Org. Chem.* 1987, *52*, 3789.

(14) Sugita, T.; Ito, H.; Nakajima, A.; Sunami, M.; Kawakatsu, A.; Suama, M.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* 1987, *60*, 721. Suama, M.; Nakajima, A.; Sugita, T.; Ichikawa, K. *Chem. Lett.* 1981, 1459.

(15) Adams, J. T.; Hauser, C. R. *J. Am. Chem. Soc.* 1944, *66*, 1220.

(16) McMahon, E. M.; Roper, J. N., Jr.; Utermohlen, W. P., Jr.; Hasek, R. H.; Harris, R. C.; Brant, J. H. *J. Am. Chem. Soc.* 1948, *70*, 2971. See also: Adam, W.; Berkessel, A.; Krimm, S. *J. Am. Chem. Soc.* 1986, *108*, 4556.

(17) Stone, K. J., Little, R. D. *J. Org. Chem.* 1984, *49*, 1849.

(18) Wilcox, C. F., Jr.; Craig, R. R. *J. Am. Chem. Soc.* 1961, *83*, 3866.

(19) Nakazaki, M.; Naemura, K.; Harada, H.; Narutaki, H. *J. Org. Chem.* 1982, *47*, 3470.

Scheme 4. Synthesis of 9[a]

30

25

14% | 4 steps

80% | c

31

a
76%

32

b
60%

33

d
74%

34

e
81%

22b

b
51%

35

f
5%

9

[a] Key: (a) CH₃MgI, Et₂O; (b) CrO₃·2py/CH₂Cl₂; (c) C₅H₆/CH₂Cl₂/ZnCl₂; (d) *hν*/Et₂O; (e) LDA/THF; (f) [(C₆H₅)₃PCH₃]Br/NaH₂/THF, -10 °C.

Scheme 5

35

36
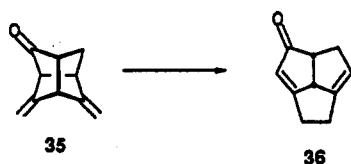
reaction at -10 °C using a mixture of triphenylphosphonium bromide and sodium amide ("instant ylide"). The low yield in the last step can be ascribed to two factors: the high volatility of 9 and the rearrangement of 9 and 35. Both compounds are composed of one or two 1,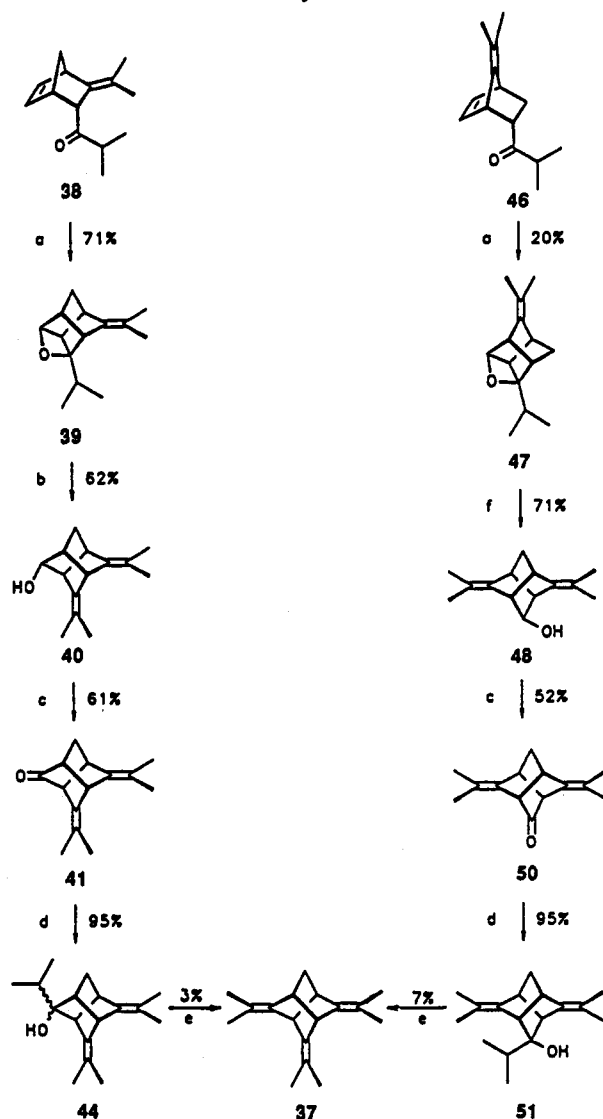5-hexadiene units within a highly strained system. As a result of these factors a Cope rearrangement to the tricyclo[5.2.1.0⁴,¹⁰]-deca-1,6-diene derivatives 13 and 36 occurs (Schemes 1 and 5).

Synthesis of 2,4,6-Triisopropylidenetricyclo-[3.3.0.0³,⁷]octane. According to the retrosynthetic analysis presented in Scheme 2 we followed two routes to synthesize the title compound 37 (Scheme 6).

Both routes use an intramolecular Paterno-Büchi reaction to complete the third carbocycle. The two oxetanes, 39 and 47, have been be prepared in 71% (39) and 20% (47) yields, respectively, using two steps. As mentioned above, the cleavage of the oxetane ring usually needs extra care. In the case of 39 we were successful with diethylaluminum 2,2,6,6-tetramethylpiperidide (DATMP).[20] In the following step, the Swern oxidation,[21] of 40

(20) Yasuda, A.; Tanaka, S.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* 1974, 96, 6513.

(21) Omura, K.; Swern, D. *Tetrahedron* 1978, 34, 1651. Mancuso, A. J.; Swern, D. *Synthesis* 1981, 165.

Scheme 6. Synthesis of 37[a]

38

a | 71%

39

b | 52%

40

c | 61%

41

d | 95%

44

3%
e

37

7%
e

51

46

a | 20%

47

f | 71%

48

c | 52%

50

d | 95%

[a] (a) *hν*/Et₂O; (b) DATMP/C₆H₆; (c) (1) (COCl)₂/DMSO, -55 °C, (2) NEt₃; (d) iPrLi/THF, 0 °C; (e) MsCl/NEt₃/CH₂Cl₂, 0 °C; (f) (1) TMS-OTf/2,6 Lu, -78 °C, (2) DBU, 25 °C, (3) (nBu)₄NF/THF, 25 °C.

Scheme 7

41

C₆D₆

42

43
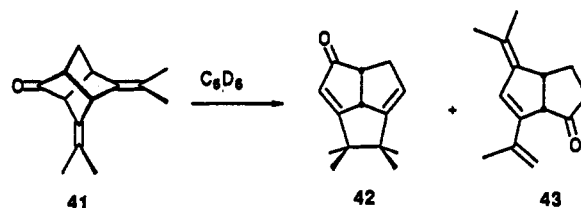
has been carried out in a 10-fold dilution to avoid the precipitation of the alkoxy sulfonium salts. From the ketone 41 we were able to grow suitable single crystals which have been investigated by X-ray crystallography.[22] The rearrangement of 41 yielded two products. Besides the anticipated Cope adduct 42 we encountered the bicyclo-[3.3.0]octane derivative 43 (Scheme 7).
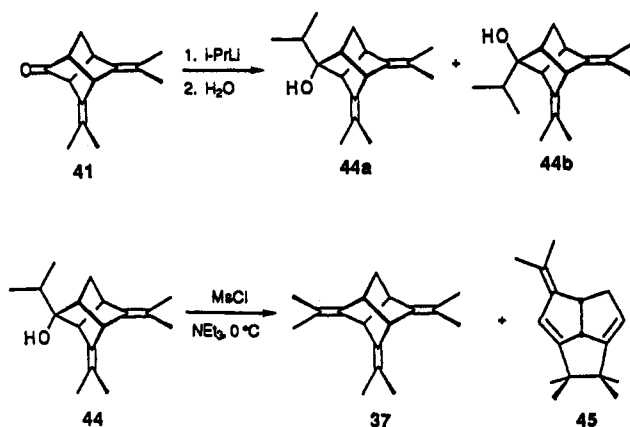
The structural assignment of 43 (mixture of s-cis- and s-trans-isomers) is based mainly on NMR data and on mechanistic considerations, as only small amounts were

(22) Siemund, V.; Irngartinger, H.; Sigwart, C.; Kissler, B.; Gleiter, R. *Acta Crystallogr.* 1993, C49, 57.

Scheme 8

Scheme 9
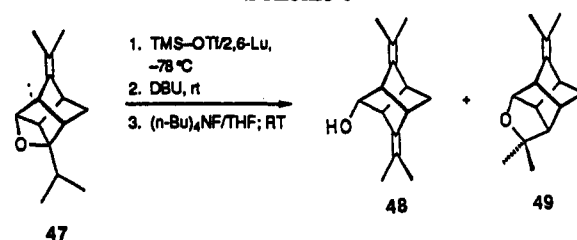
Scheme 10
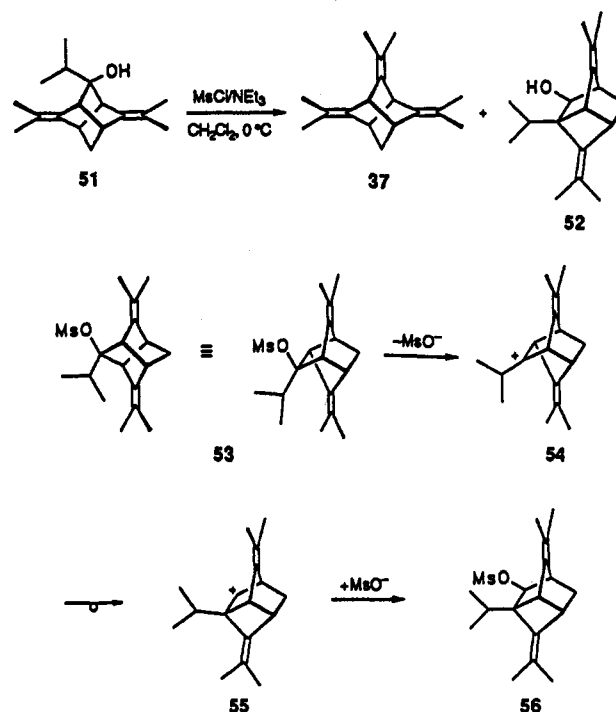
available. Surprisingly, dienone 41 turned out to be less stable than the *exo*-methylene derivative 35 due to the additional methyl groups which enable additional reaction pathways to occur. We anticipated that the next step in the reaction sequence should proceed under mild conditions, and for the introduction of the final isopropylidene group a multistep procedure was used. By addition of isopropyllithium (i-PrLi)[23] to the carbonyl bond of dienone 41 the desired carbon skeleton was completed. This reaction proceeded quantitatively at 0 °C, and after hydrolysis the epimeric alcohols 44a and 44b could be separated easily by column chromatography (Scheme 8).

The structural assignment of both compounds was based on H,H-NOESY experiments.[24] For 44b a NOE effect can be detected between the methyl protons of the isopropyl group and the allylic methyl protons at $\delta = 1.57$ and 1.54. This is consistent with close proximity of both functional groups in the structure suggested for 44b. The elimination to yield 37 from 44 was carried out with mesyl chloride and triethylamine. Besides recovered starting material (75%) we isolated 37 with small amounts of the rearranged product 45. By repeated column chromatography at 10 °C a pure fraction of the triene 37 could be obtained in poor yield (3%). The structural assignment of 37 is based on its HRMS and ^{1}H-NMR spectrum. The ^{1}H-NMR spectrum of 37 shows a reduced number of peaks due to the C_2 symmetry of this molecule. The bridgehead protons from a AA′MM′ system, and the expected ^4J coupling between the bisallylic protons at C(3) and C(5) produces a doublet of doublets at $\delta = 3.35$.

In the second route to 37 (Scheme 6) the cleavage of the oxetane ring of 47 had to be carried out by using a multistep procedure developed by Noyori et al.[25] for the conversion of 2,2-di-, tri-, and tetrasubstituted oxiranes to the corresponding allylic alcohols. Thus, the tetracyclic oxetane 47 has been treated with trimethyl silyltriflate (TMS-OTf) in the presence of 2,6-lutidine (2,6-Lu) at –78 °C (Scheme 9). Subsequent addition of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) and tetra-*n*-butylammonium fluorid ((n-Bu)$_4$$^+F^-$) led to the desired dienol 48 (71%). As a side product (21%) the ether 49 could be separated by column chromatography.

The oxidation of 48 to 50 was carried out using the Swern procedure.[21] The structural assignment of the resulting C_2 symmetrical ketone 50 is based on analytical data, and its especially simple NMR spectra (e.g., eight line ^{13}C-NMR spectrum). 50 decomposed upon heating to 40–50 °C to form mainly polymeric material. This thermal behavior could be anticipated as steric constraints prevent a Cope rearrangement, although the molecule possesses a 1,5-hexadiene unit. The tertiary alcohol 51 can be obtained in 95% yield by treatment of 50 with i-PrLi. The subsequent elimination reaction to form the desired 37 occurred in only 7% yield. As a side product of the elimination reaction we encountered the rearranged alcohol 52. The mechanism of this rearrangement has been investigated thoroughly by Sauers et al.[26,27] A possible route is outlined in Scheme 10.

Synthesis of 4′,6′,8′-Triisopropylidenespiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octane] and 4′,6′,8′-Trimethylenespiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octane]. Both title compounds were synthesized in order to study the possible stabilizing influence of substituents at the C(8) position of the tricyclic system. The synthesis of these hydrocarbons has been carried out in a straightforward manner as outlined in Scheme 11.

(23) Gilman, H.; Moore, F. W.; Baine, O. *J. Am. Chem. Soc.* 1941, *63*, 2479.

(24) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*, 3rd ed.; Georg Thieme Verlag Stuttgart: New York, 1987.

(25) Murata, S.; Suzuki, M.; Noyori, R.; *J. Am. Chem. Soc.* 1979, *101*, 2738.

(26) Sauers, R. R.; Sickles, B. R. *Tetrahedron Lett.* 1970, 1067. Sauers, R. R.; O'Hara, E. M. *J. Am. Chem. Soc.* 1974, *96*, 2510.

(27) Sauers, R. R.; Weston, C. A.; Dentz, B. I. *J. Org. Chem.* 1980, *45*, 2813.

Scheme 11. Synthesis of 67 and 68[a]

R = CH₃: **58**
(R = H: **57**)

R = CH₃: **60**
(R = H: **59**)

R = CH₃: **62**
(R = H: **61**)

R = CH₃: **64**
(R = H: **63**)

R = CH₃: **66**
(R = H: **65**)

R = CH₃: **68**
(R = H: **67**)
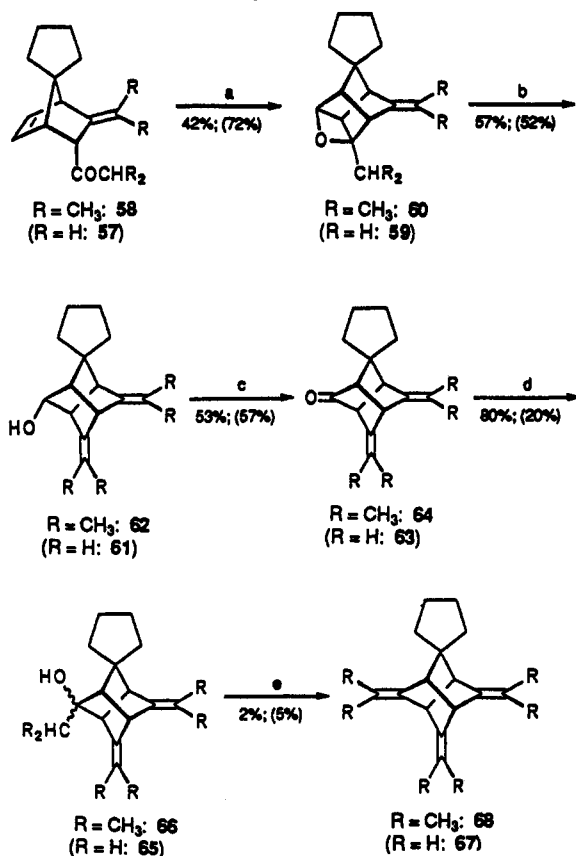
[a] Key: (a) hν/Et₂O; (b) DATMP/C₆H₆/LDA/THF); (c) (1)(COCl)₂/DMSO, –50 °C, (2) Et₃N; (d) iPrLi/THF (MeLi/Et₂O, 0 °C); (e) MsCl/NEt₃/CH₂Cl₂, 0 °C.

The starting point was the Diels–Alder reaction of spiro[4.4]nonadiene (**29**) and either acetylallene (**25**) or its tetramethyl derivative **26**. To obtain the *endo* products **57** and **58** as well as the corresponding oxetanes **59** and **60** flash chromatography was used for the purification, and the presence of small quantities of impurities was accepted to increase the amount of the desired compound. The splitting of the oxetane ring in the case of **59** was accomplished with LDA in THF[11] while **60** was cleaved with DATMP[20] in benzene. Both alcohols could be isolated in pure state after column chromatography. The ketones **63** and **64** could be obtained by Swern oxidation[21] from the alcohols. In the case of **64** single crystals could be obtained which were investigated using the X-ray technique.[22] The ketone **64** rearranged at room temperature to afford **69** and **70** in a ratio of 4:1. In the case of **63** only the triquinane derivative **71** could be detected (Scheme 12).

Reaction of the ketones with the appropriate Li-alkyls afforded **65** and **66**. As in the foregoing reactions the last step, the generation of the triene, could be carried out in only 2–5% yield. As anticipated from the previous discussion, the hydrocarbon **67** also rearranged to the corresponding triquinane derivative **72** (Scheme 12).

However, for the highly alkyl-substituted triene **68**, only slow decomposition was detected by monitoring the lifetime by means of ¹H-NMR spectroscopy. In this case no signals occurred that would have been anticipated for the corresponding rearranged triquinane derivative.

Rearrangement of Tricyclo[3.3.0.0³,⁷]octane Derivatives with Three Exocyclic Double Bonds. Except

Scheme 12

64

69 (4:1) **70**

63

71

67

72
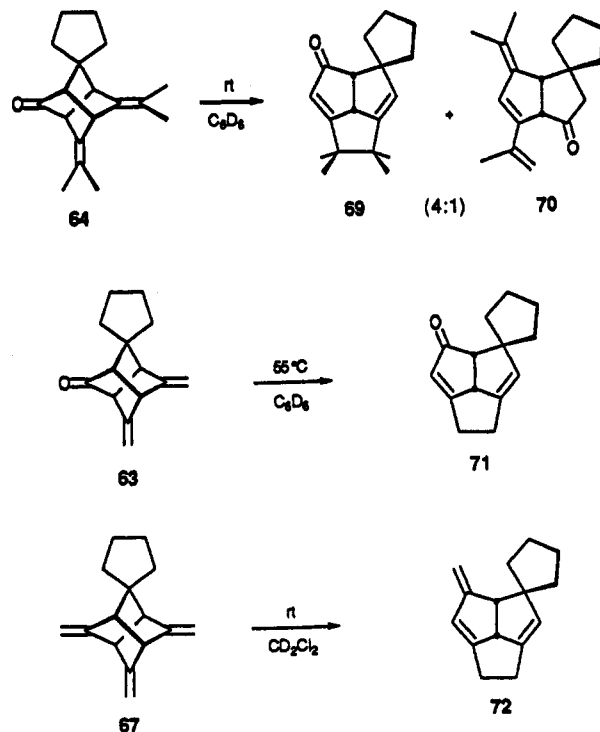
Table 1. Half-Lives of the Trienes 9, 37, 67, and 68 and the Ketones 35, 41, 63, and 64

compd	$\tau_{1/2}{}^{a}$ (min) (T (°C))[b]	solvent	products (ratio)
9	30 (30)	C₆D₆	13
67	70 (25)	CD₂Cl₂	72
37	75 (30)	C₆D₆	45
68	300 (30)	C₆D₆	c
35	31 (50)	C₆D₆	36
41	17 (50)	C₆D₆	42, 43 (1:1)
63	57 (50)	C₆D₆	71
64	40 (50)	C₆D₆	69, 70 (4:1)

[a] $\sigma_{\tau1/2}$ = ±5 min. [b] σ_{T} = ±0.5 K. [c] No rearranged products could be detected during measurement (3 h). The cited half-life refers to the vanishing signals of the educt.

for triene **68** all the tricyclo[3.3.0.0³,⁷]octane derivatives with three exocyclic double bonds mentioned thus far rearrange to the corresponding derivatives of tricyclo[5.2.1.0⁴,¹⁰]deca-1,6-diene. In Table 1 we list the recorded half-lives of the stellatrienes **9**, **37**, **67**, and **68** and the dienones **35**, **41**, **63**, and **64**. The rearranged products that could be observed are also shown. Due to the modest yield in the last step of their preparation we did not have enough materials to carry out kinetic studies. Therefore, we can discuss these results only in a qualitative manner. The data compiled in Table 1 allow the following conclusions: (1) The replacement of all *exo*-methylene groups by isopropylidene moieties in the hydrocarbons leads to a moderate stabilization (cf. **9**–**37**). Additional substitution of C(8) by sterically more demanding groups (alkyl groups) enhances the stability of the triene system (cf. **37**–**68**). (2) The substitution of C(8) by alkyl groups leads only to a pronounced stabilization of the hydrocarbons when the *exo*-methylene groups are replaced by isopropylidene moieties (cf. **9**, **67**, **68**). (3) The *exo*-methylene ketones (**35**, **63**) are more stable than the corresponding trienes (**9**, **67**). (4) The stability of the diisopropylidene ketones (**41**, **64**) is less than the dimethylene ketones (**35**, **63**).
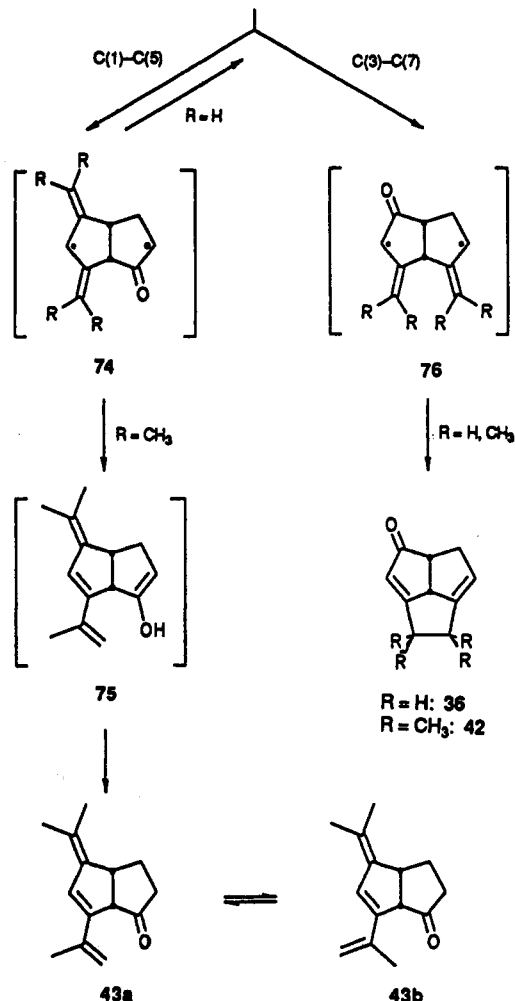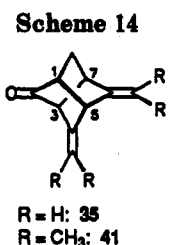
Scheme 13

73
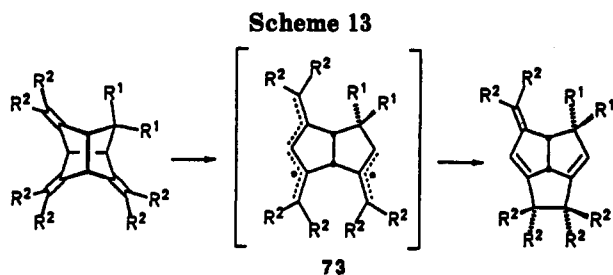
Conclusion and Discussion

Despite the thermal lability of stellatrienes we have succeeded in the preparation of the parent compound 9 and three substitution products (37, 67, 68) together with the corresponding dienones (35, 41, 50, 63, and 64). The strain inherent in these systems can be seen from the long central bonds (1.61–1.62 Å)[22] and the reduced C–C–C peripheral bond angles (93–97°).[22] From the half-lives reported in Table 1 we conclude that the existence of 10 is very difficult to prove, let alone to be isolated. At this point it should be mentioned that one attempt to synthesize stellatetraene (10) has been published by Paquette and Park.[28] The rearrangement observed for the trienes and dienones listed in Table 1 can be rationalized as a Cope rearrangement. The long central bonds and the long distance between the termini of the *exo*-methylene groups (ca. 4 Å)[22] suggest a stepwise mechanism. We assume that in the rate-determining step one of the central bonds is cleaved to yield a diradical intermediate 73 (see Scheme 13). In the second step this diradical collapses to the corresponding triquinane derivative.

We presume that in the course of the bond-breaking step the nonbonding interactions of the substituents R^1–R^2 and R^2–R^2 interfere with each other. As the steric hindrance should increase with increasing size of the functional groups, the observed differences in the half-lives of the trienes 9 ($R^1 = R^2 = H$), 37 ($R^1 = H, R^2 = CH_3$), and 68 ($R^1 = (CH_2)_4, R^2 = CH_3$) can be explained by these considerations. In the case of the dienones the cleavage of the central bonds leads to different intermediates. It results in either 74 or 76. For R = H the intermediate 74 reverts back to the starting material, and only 76 rearranges to 36. Thus, only about half of the generated intermediates lead to products. For R = CH₃ both intermediates 74 and 76 will lead to products. The formation of trienone by products 43 and 70 from the methyl-substituted derivatives 41 and 64, respectively, can also be explained in terms of the steric hindrance in the diradical intermediates 74 and 76. The nonbonded interaction would be greater in 76 in the case of R = CH₃ than that of R = H;, the side product 43 is formed via 74 (Scheme 14).

To conclude, we can say that a kinetic stabilization of stellatrienes is only possible to a certain extent as long as the main reason for the instability—the long transannular bonds—is present. On the other hand, this intrinsic strain, which we believe is mainly caused by the eclipsed conformation at the bridgehead positions, could be released by going to the twistbrendane system (e.g., 11).

Experimental Section

General Procedures. Reactions were conducted in oven-dried (120 °C) or flame-dried glassware under a positive argon atmosphere unless otherwise stated. Transfer of anhydrous

(28) Park, H.; Paquette, L. A. *J. Org. Chem.* **1980,** *45,* 5378.

Scheme 14

R = H: **35**
R = CH₃: **41**

C(1)–C(5)   C(3)–C(7)

R = H

74   **76**

R = CH₃   R = H, CH₃

75

R = H: **36**
R = CH₃: **42**

43a   **43b**

solvents or mixtures was accomplished with oven-dried syringes or cannula. Solvents were distilled and dried under argon before use: benzene, toluene, pentane, diethyl ether, and THF from sodium; dichloromethane from P₂O₅. Thin-layer chromatography (TLC) was performed on plates of silica precoated with 0.25-mm SIL G/UV₂₅₄ (Polygram). Flash columns were packed with 40–63 mesh silica gel (Kieselgel 60, Merck). Melting points were obtained on a Dr. Tottoli apparatus (Fa. Büchi) and are uncorrected.

Infrared (IR) spectral data were obtained from a Beckmann 4200, Bruker IFS-85, Perkin-Elmer 580A, or Perkin-Elmer 710B. The relative intensities of the IR bands are designated as vs, very strong; s, strong; m, medium; w, weak; br, broad. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AS 200 or Bruker WH 300. The chemical shifts are reported on the δ scale relative to the signals of the employed solvents. Coupling constants (J) are reported in hertz (Hz). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; hept, heptet; m, multiplet; br, broad, dd, doublet of doublets; dt, doublet of triplets; etc. The multiplicities of the ¹³C-NMR signals were determined by recording DEPT spectra. Ultraviolet (UV) spectra were recorded on a Varian Cary 17D, and spectral-grade *n*-hexane or CH₃CN was used as solvent. Low-resolution mass spectra were acquired on a Finnigan 3200 GLC/MS and a Hewlett-Packard HP 59970 CD GLC/MS-MSD workstation. High-

resolution (HR) mass spectra were obtained on a ZAB high-resolution mass spectrometer (Fa. Vacuum Generators) (abbreviation: DI = direct inlet). Microanalyses were carried out at the analytical section of the "Chemische Institute der Universität Heidelberg." Analytical gas chromatography (GC) was performed on a Dani 6800 and a HP 5890 A instrument connected to a Shimdazu C-R3A-integrator. Packed columns (3% OV 101 on Chromosorb WHP 100/200; 3% Carbowax on Chromosorb WHP 100/200) and a capillary column (Ultra 2, 5% PhMeSilicone, 25 m × 0.32 mm × 0.52 μm) were used with helium carrier gas and a flame ionization detector (FID).

2,4,6-Trimethylenetricyclo[3.3.0.0^{3,7}]octane (9). *endo*-2-(1-Hydroxyethyl)-3-methylenebicyclo[2.2.1]hept-5-ene (32). To a magnetically stirred solution of the conventionally prepared Grignard reagent methylmagnesium iodide (20.9 g, 125 mmol) in anhydrous ether (300 mL) was added a solution of aldehyde 31[19] (8.0 g, 60 mmol) in anhydrous ether (50 mL) dropwise. The reaction mixture was heated at reflux for 6 h, cooled, and treated with ammonium chloride solution. The aqueous layer was separated and extracted with ether. The combined organic layers were washed with brine, dried (MgSO$_4$), and evaporated. Purification of the residue by distillation afforded 32 (6.8 g, 76%) (mixture of diastereomers) as a colorless liquid: bp 82-85 °C (20 mm) (Kugelrohr); IR (neat film) ν = 3600 (br), 3074 (w), 2986 (s), 2943 (m), 2881 (m), 1654 (w), 1385 (w), 1084 (w), 895 (m), 741 (m) cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ = 6.12 (1H, dd, J_1 = 5.8 Hz, J_2 = 3.5 Hz), 6.07 (1H, dd, J_1 = 5.8 Hz, J_2 = 2.7 Hz), 5.04 (1H, s, br), 5.00 (1H, s, br), 3.21 (1H, qd, J_1 = 8.8 Hz, J_2 = 6.2 Hz), 3.18 (1H, s, br), 2.88 (1H, s, br), 2.45-2.40 (1H, md, J = 8.8 Hz), 1.7 (1H, br), 1.62 (1H, td, J_1 = 1.8 Hz, J_2 = 8.4 Hz), 1.47 (1H, d, J = 8.4 Hz), 1.20 (3H, d, J = 6.2 Hz); HRMS *m/z* calcd (M⁺) 150.1028, obsd 150.1036.

Anal. Calcd for C₁₀H₁₄O: C, 79.96; H, 9.39. Found: C, 80.10; H, 9.47.

***endo*-2-Acetyl-3-methylenebicyclo[2.2.1]hept-5-ene (33).** **Method A.** Twenty-five g (0.25 mol) of CrO₃ (dried over P₂O₅) was added to a magnetically stirred mixture of dry CH₂Cl₂ (200 mL) and dry pyridine (200 mL) at 0 °C. After being stirred at 0 °C for 0.5 h the reaction mixture was treated with a solution of 32 (6.3 g, 42 mmol) in dry CH₂Cl₂ (50 mL) and stirring continued at rt for 2 h. The CH₂Cl₂ solution was separated by decantation, and the inorganic residue was rinsed with CH₂Cl₂. The combined organic layers were washed with cold 10% hydrochloric acid, 5% sodium bicarbonate solution, and water, dried (MgSO₄), and evaporated. Purification of the residue by silica gel chromatography (elution with pentane-ether (9/1 v/v) gave 33 (3.7 g, 60%) as a colorless liquid; bp 95 °C(20 mm) (Kugelrohr); R_f (SiO₂, pentane-ether (9/1), iodine) = 0.24; IR (neat film) ν = 3056 (w), 2976 (s), 2928 (m), 2858 (w), 1709 (vs), 1683 (w), 1351 (s), 1324 (w), 1168 (w), 877 (m), 737 (s) cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ = 6.21 (1H, dd, J_1 = 5.8 Hz, J_2 = 3.1 Hz), 6.09 (1H, dd, J_1 = 5.8 Hz, J_2 = 3.1 Hz), 5.18 (1H, d, br, J = 2.2 Hz), 4.85 (1H, d, br, J = 1.8 Hz), 3.51-3.48 (1H, m), 3.32-3.25 (2H, m), 2.14 (3H, s), 1.66 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 1.52 (1H, dd, J_1 = 8.4 Hz, J_2 = 0.9 Hz); ¹³C-NMR (CDCl₃, 75.47 MHz) δ = 207.55, 148.30, 135.39, 133.95, 106.75, 58.22, 52.11, 49.95, 46.41, 28.65; UV (*n*-hexane): λ$_{max}$ (log ε) = 285 (1.52) nm; HRMS *m/z* calcd (M⁺) 148.0921, obsd 148.0905.

Anal. Calcd for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 81.03; H, 8.20.

Method B. A mixture of allene 25[12] (492 mg, 6 mmol), ZnCl₂ (60 mg, 0.6 mmol) in dry CH₂Cl₂ (40 mL), and dry ether (0.5 mL) was heated to reflux for 10 min. At -5 °C freshly distilled cyclopentadiene (960 mg, 15 mmol) was added, and the reaction mixture was stirred at -5 °C for 4 h. Water was added, and the organic layer was separated prior to drying and evaporation. Purification as described above afforded 33 (710 mg, 80%). Larger amounts of 33 were prepared in the following manner: At 0 °C 9.6 g (0.15 mol) of freshly distilled cyclopentadiene was added to acetylallene (25) (9.7 g, 0.12 mol). The reaction mixture was stirred at rt for 16 h. Purification by column chromatography afforded 16.4 g (85%) of a colorless liquid (mixture of *endo/exo*-isomeres 33/33b, GC ratio 79/21). The isomers could be isolated in pure state by repeated chromatography (elution with pentane-ether (15/1-9.1)). 33b: bp 95 °C (20 mm) (Kugelrohr); R_f (SiO₂, pentane-ether (9/1) iodine) = 0.32; IR (neat film): ν =

3056 (w), 2976 (s), 2942 (w), 1706 (s), 1646 (w), 1351 (s), 1318 (m), 1247 (w), 1240 (w), 1175 (m), 1156 (w), 882 (m), 724 (s) cm⁻¹; ¹H-NMR (CDCl₃, 200 MHz) δ = 6.18-6.16 (2H, m), 5.12 (1H, d, br, J = 2.1 Hz), 4.86 (1H, d, J = 1.8 Hz), 3.22-3.16 (1H, m), 3.12-3.07 (1H, m), 2.97-2.92 (1H, m), 2.25 (3H, s), 1.72 (1H, dm, J = 8.8 Hz), 1.55 (1H, dm, J = 8.8 Hz); ¹³C-NMR (CDCl₃, 50.32 MHz) δ = 208.25, 149.27, 137.50, 136.67, 106.39, 57.18, 50.98, 47.64, 45.91, 30.20; UV (*n*-hexane) λ$_{max}$ (log ε) = 282 (1.67) nm; MS (GC) *m/z* = 148 (M⁺).

Anal. Calcd for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 81.21; H, 8.36.

3-Methyl-8-methylene-4-oxatetracyclo-[4.2.1.0^{2,5}.0^{3,7}]nonane (22b). A solution of 33 (5.0 g, 34 mmol) in dry ether (1.0 L) was irradiated with a mercury lamp (Reaktor 400, Fa. Graentzel, Karlsruhe, Germany) for 240 h. After removal of the solvent, the residue was chromatographed on silica gel (elution with CH₂Cl₂) to give 22b (3.7 g, 74%) as a colorless liquid: bp 105 °C (20 mm) (Kugelrohr); R_f (SiO₂, CH₂Cl₂, iodine) = 0.16; IR (neat film) ν = 2960 (m), 2920 (w), 2865 (w), 1260 (s), 1070 (s), 1040 (s), 795 (s), cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 4.65 (1H, dd, J_1 = 3.9 Hz, J_2 = 2.4 Hz), 4.60 (1H, s), 4.57 (1H, s), 2.90 (1H, m), 2.77 (1H, m), 2.53 (1H, m), 2.23 (1H, m), 1.67 (2H, m), 1.35 (3H, s); ¹³C-NMR (CDCl₃, 75.47 MHz) δ = 160.2, 98.3, 96.1, 86.5, 58.4, 51.8, 45.8, 41.6, 40.5, 16.4; HRMS *m/z* calcd (M⁺) 148.0892, obsd 148.0890.

Anal. Calcd for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 81.10; H, 8.26.

4,6-Dimethylenetricyclo[3.3.0.0^{3,7}]octan-2-ol (34). To a magnetically stirred solution of diisopropylamine (42.5 mL, 0.30 mol) in anhydrous THF (900 mL) was added a 1.6 M solution of *n*-butyllithium (250 mL, 0.40 mol) in hexane at 0 °C. After the mixture was stirred for 0.5 h at 0 °C, a solution of oxetane 22b (7.4g, 0.05 mol) in anhydrous THF (100 mL) was added, and the reaction mixture was stirred for 16 h at rt. The mixture was poured into cold water (0 °C), acidified with aqueous HCl, and extracted with ether. The combined organic layers were washed with aqueous NaHCO₃ and water, dried (MgSO₄), and evaporated. Purification of the residue by silica gel chromatography (pentane-ether (9/1)) gave 34 (6.0 g, 81%) as a colorless liquid: bp 70 °C (1 mm) (Kugelrohr); R_f (SiO₂, pentane-ether (4/1), iodine) = 0.43; IR (neat film) ν = 3506 (s, br), 3066 (w), 2980 (s), 1676 (m), 1665 (m), 1407 (w), 1256 (m), 1105 (m), 1068 (s), 866 (s), 794 (w) cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ = 4.87 (1H, s), 4.69 (1H, s), 4.42 (2H, s), 3.91 (1H, dd, J_1 = 3.1 Hz, J_2 = 11.9 Hz), 2.82-2.80 (1H, m), 2.73-2.71 (1H, m), 2.56-2.52 (1H, m), 2.42-2.39 (1H, m), 2.17 (1H, d, J = 11.9 Hz, OH), 1.68 (1H, d, J = 10.2 Hz), 1.36 (1H, d, J = 10.2 Hz); ¹³C-NMR (CDCl₃, 75.46 MHz) δ = 158.06, 156.60, 100.07, 93.75, 78.32, 47.49, 46.44, 45.91, 44.59, 36.38; MS (GC) *m/z* = 148 (M⁺); UV (*n*-hexane): λ$_{max}$ (log ε) = 213 (3.94) nm.

Anal. Calcd for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 80.93; H, 8.29.

4,6-Dimethylenetricyclo[3.3.0.0^{3,7}]octan-2-one (35). CrO₃ (25.0 g, 0.25 mol) was added at 0 °C to a magnetically stirred solution of dry pyridine (79 g, 1.0 mol) in dry CH₂Cl₂ (1.3 L). After the reaction mixture was stirred at 0 °C for 0.5 h, a solution of dienol 34 (5.3 g, 0.036 mol) in dry CH₂Cl₂ (100 mL) was added and stirring continued for 1.5 h at 15 °C. The CH₂Cl₂ solution was separated by decantation, and the dark residue was rinsed with CH₂Cl₂. The combined CH₂Cl₂ extracts were washed with cold 4% hydrochloric acid, 5% sodium bicarbonate solution, and water, dried (Na₂SO₄), and evaporated at 10 °C. Purification of the residue by silica gel chromatography (elution with pentane-ether (10/1)) at 0 °C gave 35 (2.7 g, 51%) as a colorless solid which could be crystallized from pentane-ether (12/1) at -20 °C: mp 32-34 °C; R_f (SiO₂, pentane-ether (4/1), iodine) = 0.55; IR (CCl₄) ν = 3000 (w), 2870 (w), 1780 (vs), 1699 (w), 1686 (w), 1669 (w), 882 (s) cm⁻¹; ¹H-NMR (CD₂Cl₂, 300 MHz) δ = 4.80 (1H, s), 4.73 (1H, s), 4.70 (1H, s), 4.65 (1H, s), 3.22-3.18 (1H, m), 3.02-2.98 (1H, m), 2.76-2.72 (1H, m), 2.59-2.55 (1H, m), 1.79 (1H, d, J = 11.1 Hz), 1.72 (1H, d, J = 11.1 Hz); ¹³C-NMR (CDCl₃, 75.46 MHz) δ = 205.58, 155.49, 148.27, 101.00, 97.76, 53.16, 49.62, 48.72, 43.63, 36.50; UV (CH₃CN) λ$_{max}$ (log ε) = 295 (489) nm; HRMS *m/z* calcd (M⁺) 146.0730, obsd 146.0742.

2,4,6-Trimethylenetricyclo[3.3.0.0^{3,7}]octane (9). At 0 °C a mixture of 4.2 g of methyltriphenylphosphonium bromide/NaNH₂ (Instant Ylide, ≃ 10 mmol phosphonium salt) in dry THF (100

mL) was stirred for 0.5 h. At –10 °C a solution of dienone 35 (730 mg, 5.0 mmol) in dry THF (10 mL) was added, and the reaction mixture was stirred for 16 h at –10 °C. After addition of pentane (100 mL), the mixture was filtered on silica gel (elution with pentane) at –8 °C. The filtrate was evaporated at 10 °C, and the residue was chromatographed on silica gel (elution with *n*-pentane) at –8 °C to yield 3 (36 mg, 5%) as a colorless, volatile liquid: R_f (SiO$_2$, pentane, iodine) = 0.40; ^{1}H-NMR (CD$_2$Cl$_2$, 200 MHz, 263 K) δ = 4.46 (2H, s, br), 4.45 (2H, s, br), 4.36 (2H, s, br), 2.93 (2H, t, br, J = 2.8–2.7 Hz), 2.78–2.74 (2H, m), 1.58 (2H, t, br, J = 1.7 Hz); ^{13}C-NMR (CD$_2$Cl$_2$, 50.32 MHz, 263 K) δ = 159.19*, 156.44, 94.80*, 94.33, 50.51*, 44.99*, 42.58 (* = double intensity).

2,4,6-Triisopropylidenetricyclo[3.3.0.0^{3,7}]octane (37) via Dienone 41. endo-2-Isobutyryl-3-isopropylidenebicyclo-[2.2.1]hept-5-ene (38). A mixture of freshly distilled cyclopentadiene (10.0 g, 0.15 mol) and allene 26[13] (13.8 g, 0.10 mol) was stirred at 50 °C for 40 h, and addition of cyclopentadiene (3.3 g, 0.05 mol) occurred after 16 and 32 h. Purification of the cold reaction mixture by silica gel chromatography (elution with pentane–ether (12/1–9/1)) gave 38 (10.8 g, 56%) as a colorless liquid: R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.15; IR (film) ν = 2962 (s), 2924 (s), 2864 (m), 1709 (s), 1688 (w), 1463 (w), 1443 (w), 1377 (w), 1367 (w), 1036 (m), 516 (m) cm^{-1}; ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 6.22 (1H, dd, J_1 = 5.5 Hz, J_2 = 3.1 Hz), 5.77 (1H, dd, J_1 = 5.5 Hz, J_2 = 2.7 Hz), 3.72–3.68 (1H, m), 3.51–3.47 (1H, m), 3.25–3.21 (1H, m), 2.81 (1H, hept, J = 6.9 Hz), 1.74 (3H, d, J = 1.4 Hz), 1.59 (1H, dm, J = 8.0 Hz), 1.43 (1H, dm, J = 8.0 Hz), 1.39 (3H, s), 1.13 (3H, d, J = 6.9 Hz), 1.06 (3H, d, J = 6.9 Hz); ^{13}C-NMR (CDCl$_3$, 75.47 MHz): δ = 212.73, 135.47, 132.94, 131.97, 123.05, 54.43, 49.92, 47.92, 47.00, 39.87, 23.09, 21.08, 19.56, 18.12; MS (GC, relative percent) m/z = 204 (M$^+$, 45); UV (*n*-hexane) λ_{max} (log ϵ) = 285 (1.89) nm.

Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87. Found: C, 82.97; H, 9.82.

3-Isopropyl-8-isopropylidene-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]-nonane (39). A solution of *endo*-ketone 38 (6.1 g, 30 mmol) in dry ether (1.0 L) was irradiated with a mercury lamp (Reaktor 400, Fa. Graentzel, Karlsruhe, Germany) for 48 h at rt. After evaporation the residue was chromatographed on silica gel (elution with pentane–ether (12/1–9/1)) to give 39 (4.4 g, 71%), which could be crystallized at –20 °C from pentane–ether (20/1) as colorless crystals: mp 31 °C (sealed tube); R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.21; IR (CDCl$_3$) ν = 3002 (s), 2956 (s), 2924 (s), 2864 (s), 1442 (w), 1291 (w), 1277 (w), 1258 (m), 1116 (m), 1063 (w), 1026 (m), 976 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 4.46 (1H, dd, J_1 = 3.6 Hz, J_2 = 2.2 Hz), 2.93–2.85 (2H, m), 2.65–2.60 (1H, m), 2.25–2.21 (1H, m), 1.74 (1H, hept, J = 7.0 Hz), 1.55 (3H, s), 1.51 (3H, s), 1.42 (1H, dd, J_1 = 9.9 Hz, J_2 = 1.7 Hz), 1.35 (1H, dd, J_1 = 9.9 Hz, J_2 = 2.2 Hz), 1.08 (3H, d, J = 7.0 Hz), 1.05 (3H, d, J = 7.0 Hz); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 145.75, 114.47, 102.13, 85.61, 55.88, 46.80, 45.97, 40.41, 38.21, 28.05, 20.08, 19.67, 18.68, 16.48; MS (GC, relative percent) m/z = 204 (M$^+$, 7); UV (*n*-hexane) λ_{max} (log ϵ) = 206 (3.80) nm.

Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87. Found: C, 82.16; H, 9.89.

4,6-Diisopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-ol (40). *n*-Butyllithium (60 mL of a 1.6 M solution in hexane, 96 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethyl-piperidine (16 mL, 96 mmol) in dry benzene (800 mL) at 6 °C. At 0 °C the reaction mixture was stirred for 10 min, treated with Et$_2$AlCl (96 mL of a 1.0 M solution in hexane, 96 mmol), and stirred for 0.5 h. A solution of oxetane 39 (7.4 g, 36 mmol) in dry benzene (200 mL) was added, and the mixture was stirred at rt for 1 h before being poured into a mixture of ice–water (800 mL) and concd HCl (120 mL) and then extracted with ether (3×). The combined organic layers were washed with aqueous NaHCO$_3$ (5%) and brine, dried (MgSO$_4$), and evaporated. Purification of the residue by silica gel chromatography (elution with pentane–ether (9/1–4/1)) gave 40 (4.6 g, 62%), which could be crystallized at –20 °C from pentane–ether (12/1) as colorless crystals: mp 43–44 °C (sealed tube); R_f (SiO$_2$, pentane–ether (4/1), iodine) = 0.26; IR (CDCl$_3$) ν = 3486 (w), 3000 (m), 2966 (s), 2908 (s), 2850 (m), 1444 (w), 1411 (w), 1288 (w), 1257 (m), 1186 (m), 1175 (w), 1123 (w), 1079 (m), 1058 (s) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.88 (1H, dd, J_1 = 12.2 Hz, J_2 = 3.0 Hz), 3.09–3.06 (1H, m), 2.66–2.57 (2H, m), 2.30–2.27 (1H, m), 1.96 (1H, d, J = 12.2 Hz,

OH), 1.57 (3H, s), 1.54 (3H, s), 1.46 (3H, s), 1.42 (3H, s), 1.31 (1H, dd, J_1 = 9.8 Hz, J_2 = 2.4 Hz), 1.09 (1H, dd, J_1 = 9.8 Hz, J_2 = 2.9 Hz); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 144.03, 141.45, 116.55, 108.40, 79.65, 46.91, 45.15, 42.03, 40.16, 36.37, 20.18, 20.00, 19.80, 19.40; MS (DI, relative percent) m/z = 204 (M$^+$, 6); UV (*n*-hexane) λ_{max} (log ϵ) = 220 (4.02) nm.

Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87. Found: C, 82.30; H, 10.10.

4,6-Diisopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (41). A magnetically stirred solution of oxalyl chloride (2.3 mL, 27 mmol) in dry CH$_2$Cl$_2$ (60 mL) was treated with dry DMSO (3.9 mL, 55 mmol) at –50 to –60 °C. After the mixture was stirred for 2 min, a solution of dienol 40 (4.6 g, 23 mmol) in dry CH$_2$Cl$_2$ (25 mL) was added dropwise at –50 to –60 °C. The reaction mixture was stirred for 15 min, treated with triethylamine (16 mL, 115 mmol), and allowed to warm to rt before being poured into cold aqueous HCl (2%). Extraction was effected with CH$_2$Cl$_2$ (2×), and the combined CH$_2$Cl$_2$ solutions were washed with aqueous NaHCO$_3$ (5%) and brine, dried (MgSO$_4$), and evaporated. Purification of the residue by silica gel chromatography (elution with pentane–ether (9/1)) gave 41 (2.8 g, 61%), which could be crystallized at –20 °C from the pentane–ether (20/1) as colorless crystals: mp 65 °C (sealed tube); R_f (SiO$_2$, pentane–ether (12/1), iodine) = 0.14; IR (CDCl$_3$) ν = 3020 (m), 3006 (m), 2968 (m), 2966 (s), 2908 (s), 2864 (s), 2850 (m), 1751 (vs), 1442 (w), 1270 (w), 1192 (m), 1141 (m), 1016 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 200 MHz, 283 K) δ = 3.30–3.25 (1H, m), 2.79–2.73 (2H, m), 2.34–2.28 (1H, m), 1.52 (3H, s), 1.52–1.44 (1H, m), 1.48 (3H, s), 1.45 (3H, s), 1.40 (3H, s), 1.22 (1H, ddd, J_1 = 10.7 Hz, J_2 = 2.9 Hz, J_3 = 0.7 Hz); ^{13}C-NMR (C$_6$D$_6$, 50.32 MHz, 283K) δ = 204.12, 141.37, 133.69, 117.54, 112.64, 50.22, 48.99, 42.87, 40.62, 36.13, 20.08, 20.00, 20.06, 19.83, 19.60; MS (DI, relative percent) m/z = 202 (M$^+$, 24); UV (*n*-hexane) λ_{max} (log ϵ) = 202 (4.11), 214 (4.02 sh), 298 (2.85), 306 (2.79, sh) nm.

Anal. Calcd for C$_{14}$H$_{18}$O: C, 83.12; H, 8.97. Found: C, 83.30; H, 9.12.

4,6-Diisopropylidene-syn-2-hydroxy-2-isopropyltricyclo-[3.3.0.0^{3,7}]octane (44a) and 4,6-Diisopropylidene-anti-2-hydroxy-2-isopropyltricyclo[3.3.0.0^{3,7}]octane (44b). Freshly prepared isopropyllithium (27 mL of a 0.3 M solution in *n*-pentane)[23] was added dropwise to a magnetically stirred solution of dienone 41 (1.5 g, 7.4 mmol) in dry THF (100 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, poured into cold 2% aqueous HCl, and extracted with ether (2×). The combined organic layers were washed with 5% aqueous NaHCO$_3$ and brine, dried (MgSO$_4$), and evaporated. Purification of the residue by silica gel chromatography (elution with pentane–ether (12/1) gave 44a (875 mg, 48%) and 44b (860 mg, 47%), which both could be crystallized at –20 °C from pentane–ether (12/1) as colorless solids. 44a: mp 81 °C (sealed tube); R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.39; IR (KBr) ν = 3498 (s), 3002 (s), 2988 (m), 2968 (s), 2952 (s), 2900 (m), 2862 (m), 2846 (m), 1443 (w), 1378 (m), 1366 (m), 1356 (m), 1286 (m), 1264 (w), 1171 (m), 1163 (w), 1147 (m), 1007 (s), 971 (w), 583 (w), 571 (w), 536 (w), 502 (m), 483 (m), 479 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.22–3.18 (1H, m), 2.71–2.67 (1H, m), 2.52–2.49 (1H, m), 2.24–2.20 (1H, m), 2.10 (1H, d, J = 1.5 Hz, OH), 1.89 (1H, hept d, J_1 = 6.7 Hz, J_2 = 1.2 Hz), 1.83 (1H, dd, J_1 = 10.6 Hz, J_2 = 2.3 Hz), 1.58 (3H, s), 1.53 (3H, s), 1.51 (3H, s), 1.42 (3H, s), 1.16 (3H, d, J = 6.7 Hz), 1.12 (3H, d, J = 6.7 Hz), 1.11 (1H, dd, J_1 = 10.6 Hz, J_2 = 2.7 Hz); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 144.22, 142.10, 114.84, 107.59, 86.18, 49.52, 47.65, 44.22, 42.93, 35.44, 30.49, 20.02, 19.94, 19.46, 19.40, 18.07, 15.56; MS (GC, relative percent) m/z = 246 (M$^+$, 1); UV (*n*-hexane) λ_{max} (log ϵ) = 220 (3.99) nm.

Anal. Calcd for C$_{17}$H$_{26}$O: C, 82.87; H, 10.64. Found: C, 82.60; H, 10.70.

44b: mp 113 °C (sealed tube), hygroscopic solid; R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.12; IR (CDCl$_3$) ν = 3596 (m), 3000 (s), 2958 (s), 2920 (s), 2866 (s), 2848 (s), 1441 (w), 1263 (w), 1237 (w), 1226 (w), 1197 (m), 1176 (m), 1121 (w), 1040 (w), 1029 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.14–3.10 (1H, m), 2.95–2.90 (1H, m), 2.65 (1H, dd, J_1 = 9.6 Hz, J_2 = 2.6 Hz), 2.42–2.38 (1H, m), 2.15–2.11 (1H, m), 1.88 (1H, hept, J = 6.8 Hz), 1.63 (3H, s), 1.57 (3H, s), 1.54 (6H, s), 1.30 (1H, s, dd, J_1 = 9.6 Hz, J_2 = 2.5 Hz), 1.05 (1H, s, 0.88 (3H, d, J = 6.8 Hz), 0.86 (3H, d, J = 6.8 Hz); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 144.60, 140.90, 110.24, 106.53, 87.78, 49.84, 46.29, 45.41, 43.57, 37.25, 31.38, 21.12,

20.18, 19.47, 19.44, 17.55, 17.11; MS (DI, relative percent) m/z = 246 (M$^+$, 3); UV (n-hexane) λ_{max} (log ϵ) = 222 (4.02) nm.

Anal. Calcd for C$_{17}$H$_{26}$O: C, 82.87; H, 10.64. Found: C, 82.73; H, 10.65.

2,4,6-Triisopropylidenetricyclo[3.3.0.0^{3,7}]octane (37). A solution of methanesulfonyl chloride (160 mg, 1.4 mmol) in dry CH$_2$Cl$_2$ (4 mL) and a solution of triethylamine (1 mL, 7.2 mmol) in dry CH$_2$Cl$_2$ (4 mL) were added dropwise at the same time to a magnetically stirred solution of dienol 44a (165 mg, 0.67 mmol) in dry CH$_2$Cl$_2$ (4 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h before evaporation was effected at 15 °C. The residue was extracted with ether, and the extracts were filtered and evaporated. Purification of the residue by silica gel chromatography (elution with n-pentane) at 10 °C gave 37 (5 mg, 3%) as a colorless liquid. Unreacted dienol 44a (123 mg, 75%) could be recovered by elution with pentane–ether (12:1). 37: R_f (SiO$_2$, pentane, iodine) = 0.34; IR (CD$_2$Cl$_2$) ν = 2954 (s), 2920 (vs), 2848 (s), 1445 (m) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.36 (2H, t, br, J = 3 Hz), 2.96–2.91 (2H, m), 1.68 (6H, s, br), 1.61 (6H, s), 1.58 (6H, s, br), 1.52–1.48 (2H, m); UV (n-hexane) λ_{max} (log ϵ) = 198 (4.23), 224 (3.93, sh); HRMS (DI) m/z calcd (M$^+$) 228.1872, obsd 228.1837.

2,4,6-Triisopropylidenetricyclo[3.3.0.0^{3,7}]octane (37) via Dienone 50. 3-Isopropyl-9-isopropylidene-4-oxatetracyclo-[4.2.1.0^{2,5}.0^{3,7}]nonane (47). (1) Cycloaddition Step. A mixture of 6,6-dimethylpentafulvene (28)[17] (28.0 g, 0.26 mol) and isopropyl vinyl ketone (27)[29] (26.0 g, 0.26 mol) was stirred at rt for 3 d. Purification by silica gel chromatography (elution with pentane–ether (25/1–9/1)) gave 41.0 g of a colorless liquid, which contained mainly the $endo/exo$-isomers 46 (R_f[endo-46] (SiO$_2$, pentane–ether (25/1), iodine) = 0.26, R_f[exo-46] (SiO$_2$, pentane–ether (25/1), iodine) = 0.31) in addition to other unknown impurities. This material was used in the following photochemical step. (2) **Photocyclization.** A solution of 46 (10.0 g, raw material) in dry ether (2.5 L) was irradiated with a medium-pressure mercury lamp (Hanovia 450, $\lambda \geq 280$ nm) until conversion was complete. After removal of the solvent, the residue was chromatographed on silica gel (elution with pentane–ether (12/1) to give 47 (2.6 g, 20% over two steps), which could be crystallized at –20 °C from pentane–ether (9/1) as colorless crystals: mp 43 °C (sealed tube); R_f (SiO$_2$, pentane–ether (12/1), iodine) = 0.30; IR (CDCl$_3$) ν = 3002 (s), 2956 (s), 2926 (s), 2868 (s), 1442 (m), 1279 (m), 1264 (m), 1240 (w), 1167 (w), 1123 (w), 1078 (m), 947 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 4.41 (1H, dd, J_1 = 3.9 Hz, J_2 = 2.3 Hz), 3.13–3.08 (1H, m), 2.91–2.86 (1H, m), 2.43–2.39 (1H, m), 2.27–2.23 (1H, m), 1.66 (1H, hept, J = 6.9 Hz), 1.55 (1H, dd, J_1 = 10.2 Hz, J_2 = 2.2 Hz), 1.53 (6H, s), 1.47 (1H, ddd, J_1 = 10.2 Hz, J_2 = 2.5 Hz, J_3 = 1.0 Hz), 1.12 (3H, d, J = 6.9 Hz), 1.04 (3H, d, J = 6.9 Hz); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 144.52, 114.06, 103.14, 82.69, 55.35, 47.37, 45.14, 40.76, 37.87, 28.74, 19.63, 19.49, 19.12, 16.00; MS (GC, relative percent) m/z = 204 (M$^+$, 2).

Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87. Found: C, 82.47; H, 10.03.

4,8-Diisopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-ol (48) and 5,5-Dimethyl-9-isopropylidene-4-oxatetracyclo[5.2.1.0^{2,6}.0^{3,8}]-decane (49). A mixture of trimethyl silyltriflate (75 mL of a 0.1 M solution in dry toluene, 7.5 mmol) and 2,6-lutidine (75 mL of a 0.1 M solution in dry toluene, 7.5 mmol) was added dropwise to a stirred solution of oxetane 47 (1.0 g, 4.9 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 3 h, treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU, 0.75 g, 4.9 mmol) at 0 °C, stirred at rt for 14 h, treated with tetra-n-butylammonium fluoride (6.8 mL of a 1.1 M solution in THF, 7.5 mmol), and stirred at rt for 24 h. The mixture was washed with 5% aqueous HCl, 5% aqueous NaHCO$_3$, and brine prior to drying (MgSO$_4$) and evaporation. Purification of the residue by silica gel chromatography (elution with pentane–ether (14/1–12/1)) provided 48 (710 mg, 71%) as colorless crystals (from pentane–ether (12/1) at –20 °C) and 49 (212 mg, 21%) as a colorless liquid: 48: mp 67 °C (sealed tube); R_f (SiO$_2$, pentane–ether (12/1), iodine) = 0.18; IR (CDCl$_3$) ν = 3486 (m), 2998 (s), 2948 (s), 2908 (s), 2860 (s), 1441 (m), 1400 (m), 1257 (m), 1149 (s), 1113 (w), 1047 (s), 523 (m) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.84 (1H, dd, J_1 = 12.4 Hz, J_2 = 2.8 Hz), 2.73–2.70 (1H, m), 2.68–2.56 (3H, m), 2.08 (1H, d, J = 12.4 Hz), 1.55 (3H, s), 1.54 (3H, s), 1.51 (3H, s), 1.50 (3H, s), 1.40 (1H, dd, J_1 = 8.9 Hz, J_2 = 2.4 Hz), 1.30 (1H, dd, J_1 = 8.9

Hz, J_2 = 2.4 Hz); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 144.96, 142.38, 117.43, 111.76, 78.33, 48.67, 45.91, 42.07, 41.56, 37.71, 20.40, 19.79, 19.51, 19.33; MS (GC, relative percent) m/z = 204 (M$^+$, 63); UV (n-hexane) λ_{max} (log ϵ) = 214 (2.76), 218 (2.75, sh), 226 (2.74, sh) nm.

Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87. Found: C, 82.19; H, 9.67.

49: R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.31; IR (film); ν = 2968 (s), 2918 (m), 2866 (m), 1374 (w), 1368 (w), 1360 (m), 1315 (m), 1173 (w), 1165 (w), 1075 (w), 1063 (s), 814 (w), cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.99–3.97 (1H, m), 2.64–2.61 (1H, m), 2.59–2.57 (1H, m), 2.48–2.43 (1H, m), 2.22–2.20 (1H, m), 1.77–1.75 (1H, m), 1.53 (3H, s), 1.48 (3H, s), 1.41 (1H, dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz), 1.32 (1H, dd, J_1 = 9.2 Hz, J_2 = 2.7 Hz), 1.28 (3H, s), 1.10 (3H, s); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 143.59, 111.34, 85.72, 79.14, 60.89, 47.54 (CH), 44.33, 43.49, 38.86, 37.38, 29.27, 26.53, 19.56, 19.30; MS (GC, relative percent) m/z = 204 (M$^+$, 4); UV (n-hexane) λ_{max} (log ϵ) = 200 (3.99) nm.

Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87. Found: C, 82.35; H, 9.63.

4,8-Diisopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (50). The Swern oxidation[21] of dienol 48 was accomplished in the same way as the oxidation of dienol 40. Thus, 48 (510 mg, 2.5 mmol) yielded 50 (263 mg, 52%) as a colorless solid (from pentane–ether (12/1) at –20 °C): mp (not determinable because of decomposition); R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.26; IR (CDCl$_3$) ν = 3002 (m), 2962 (m), 2928 (s), 2908 (s), 2866 (m), 2850 (m), 1746 (vs), 1724 (s) 1701 (m), 1442 (w), 1270 (w), 1153 (m), 1142 (w), 575 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 2.91 (4H, s, br), 1.48 (12H, s), 1.39 (2H, s, br); ^{13}C-NMR (C$_6$D$_6$, 50.32 MHz) δ = 196.49, 137.52*, 118.63*, 52.80*, 41.97*, 39.46, 20.30*, 19.65* (* = double intensity); MS (DI, relative percent) m/z = 202 (M$^+$, 24); UV (n-hexane) λ_{max} (log ϵ) = 216 (4.31), 302 (2.46), 312 (2.40, sh) nm.

Anal. Calcd for C$_{14}$H$_{18}$O: C, 83.12; H, 8.97. Found: C, 83.06; H, 9.01.

2-Isopropyl-4,8-diisopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-ol (51). The reaction of dienone 50 with isopropyllithium was accomplished in the same way as in the case of dienone 41. Thus, 263 mg of 50 (1.3 mmol) afforded 304 mg (95%) of 51 as colorless crystals (from pentane–ether (12/1) at –20 °C): mp 59.5–60.5 °C (sealed tube); R_f (SiO$_2$, pentane–ether (12/1), iodine) = 0.40; IR (CDCl$_3$) ν = 3472 (m), 2996 (s), 2956 (s), 2926 (s), 2908 (s), 2864 (s), 1442 (w), 1359 (w), 1300 (w), 1270 (w), 1196 (s), 1187 (w), 1159 (w), 1142 (w), 1011 (m), 504 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 2.68–2.61 (4H, m), 2.34 (1H, d, J = 1.7 Hz), 2.08 (1H, hept d, J_1 = 6.8 Hz, J_2 = 1.7 Hz), 1.65 (3H, s), 1.55 (3H, s), 1.50 (3H, s), 1.48 (3H, s), 1.43 (1H, d, br, J = 8.8 Hz), 1.37 (1H, dd, J_1 = 8.8 Hz, J_2 = 1.9 Hz), 1.18 (3H, d, J = 6.8 Hz), 1.15 (3H, d, J = 6.8 Hz); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 146.14, 144.24, 115.88, 111.48, 86.22, 50.97, 48.71, 42.65, 42.21, 41.05, 29.98, 21.17, 20.27, 19.06, 18.86, 18.11, 17.41; MS (DI, relative percent) m/z = 246 (M$^+$, 8); UV (n-hexane) λ_{max} (log ϵ) = 198 (4.22), 214 (4.16, sh) nm.

Anal. Calcd for C$_{17}$H$_{26}$O: C, 82.87; H, 10.64. Found: C, 83.01; H, 10.68.

2,4,6-Triisopropylidenetricyclo[3.3.0.0^{3,7}]octane (37) and 3-Isopropyl-4,7-diisopropylidenetricyclo[3.2.1.0^{4,6}]octan-2-ol (52). A solution of methanesulfonyl chloride (183 mg, 1.6 mmol) in dry CH$_2$Cl$_2$ (10 mL) and a solution of triethylamine (0.46 mL, 3.2 mmol) in dry CH$_2$Cl$_2$ (10 mL) was added slowly to a magnetically stirred solution of dienol 51 (197 mg, 0.80 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 4 h prior to evaporation at 15 °C. Extraction of the residue was effected with ether, and the extracts were filtered and evaporated. Purification of the residue by silica gel chromatography (elution with n-pentane) at 10 °C provided 12 mg (7%) of 37 (identified by ^{1}H-NMR spectrum). Unreacted dienol 51 (120 mg, 61%) and rearranged dienol 52 (30 mg, 15%, colorless crystals from pentane) could be eluted with pentane–ether (12/1). 52: mp 69 °C (sealed tube); R_f (SiO$_2$, pentane–ether (12/1), iodine) = 0.17; IR (CDCl$_3$) ν = 3554 (w), 2922 (s), 2850 (s), 1441 (m), 1361 (m), 1244 (m), 1170 (m), 1151 (m), 1141 (w), 1116 (w), 1056 (m), 1025 (s), 527 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.87 (1H, d, J = 9.6 Hz), 2.85–2.74 (3H, m), 2.17 (1H, hept. br, J = 6.7 Hz), 1.65 (1H, dd, J_1 = 11.2 Hz, J_2 = 4.2 Hz), 1.60 (6H, s), 1.56 (3H, s), 1.46 (3H,

s), 1.36 (1H, d, $J = 11.0$Hz), 1.14 (1H, s), 1.12 (3H, d, $J = 6.9$Hz), 1.08 (3H, d, $J = 6.5$ Hz); ^{13}C-NMR (C_6D_6, 75.47 MHz) $\delta = 142.91$, 142.03, 119.36, 117.09, 83.14, 64.77, 46.89, 38.51, 36.01, 35.73, 28.35, 21.58, 20.86, 20.79, 20.28, 19.87, 18.88; MS (DI, relative percent) m/z = 246 (M^+, 7); UV (*n*-hexane) λ_{max} (log ϵ) = 200 (4.47) nm.

Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.84; H, 10.71.

4′,6′,8′-Trimethylenespiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octane] (67). endo-2-Acetyl-3-methylenespiro[bicyclo[2.2.1]hept-5-ene-7,1′-cyclopentane] (57). A mixture of spiro[4.4]nona-2,5-diene (29)[18] (34.0 g, 0.28 mol) and acetylallene 25[12] (20.0 g, 0.24 mol) was stirred at rt for 3 d. Purification of the reaction mixture by silica gel chromatography (elution with pentane–ether (15/1–9/1)) gave 57 (16.0 g, 33%) as a colorless liquid with few impurities (mainly 25): R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.18; ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 6.18–6.14 (1H, m), 6.04–6.00 (1H, m), 5.16 (1H, d, br, $J = 1.9$ Hz), 4.87 (1H, d, $J = 1.3$ Hz), 3.48–3.45 (1H, m), 2.86–2.77 (2H, m), 2.11 (3H, s), 1.7–1.2 (8H, m); MS (GC, relative percent) m/z = 202 (M^+, 2).

3′-Methyl-8′-methylene-4′-oxaspiro[cyclopentane-1,9′-tetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane] (59). A solution of 2.8 g of 57 in dry ether (2.5 L) was irradiated with a medium-pressure mercury lamp (Hanovia 450, $\lambda \geq 280$nm) for 18 h. After removal of the solvent, the residue was chromatographed on silica gel (elution with CH$_2$Cl$_2$) to give 59 (2.0 g, 72%) as a colorless liquid: R_f (SiO$_2$, CH$_2$Cl$_2$, iodine) = 0.31; IR (film): ν = 2958 (s), 2854 (m), 1676 (m), 1447 (w), 1379 (m), 1099 (m), 972 (m), 873 (m), 863 (m), 850 (w), 548 (w), 484 (w) cm^{-1}; ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 4.71 (1H, dd, $J_1 = 3.5$ Hz, $J_2 = 2.2$ Hz), 4.64 (1H, s), 4.59 (1H, s), 3.03–2.99 (1H, m), 2.54–2.50 (1H, m), 2.47–2.43 (1H, m), 1.90–1.87 (1H, m), 1.65–1.25 (8H, m), 1.38 (3H, s); ^{13}C-NMR (CDCl$_3$, 75.47 MHz) δ = 158.97, 99.80, 95.75, 85.47, 61.78, 60.10, 57.63, 53.93, 51.02, 32.76, 31.77, 25.18, 24.81, 16.64; MS (GC, relative percent) m/z = 202 (M^+, 8); UV (*n*-hexane): λ_{max} (log ϵ) = 202 (3.78) nm.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.11; H, 9.07.

6′,8′-Dimethylenespiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octan]-4′-ol (61). The cleavage of the oxetane ring of 59 induced by LDA was accomplished in the same way as in the case of oxetane 22b. Thus, 2.0 g of 59 (10.0 mmol) yielded 61 (1.1 g, 52%) as a colorless liquid after purification by silica gel chromatography (pentane–ether (9/1)): R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.11; IR (film): ν = 3512 (w, br), 2978 (m), 2942 (s), 2854 (m), 1666 (w), 1237 (w), 1112 (m), 1066 (m), 1052 (m), 866 (m), 555 (w), 531 (w), 525 (w) cm^{-1}; ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 4.85 (1H, s), 4.66 (1H, s), 4.51 (1H, s), 4.40 (1H, s), 4.32 (1H, dd, $J_1 = 11.8$ Hz, $J_2 = 3.1$ Hz), 2.78–2.75 (1H, m), 2.68–2.64 (1H, m), 2.42–2.39 (1H, m), 2.21 (1H, d, $J = 11.8$ Hz), 2.17–2.14 (1H, m), 1.81–1.20 (8H, m); ^{13}C-NMR (CDCl$_3$, 75.47 MHz) δ = 157.22, 157.04, 100.00, 96.38, 74.70, 59.95, 56.24, 53.36, 51.15, 49.76, 36.15, 35.29, 26.54, 25.43; MS (GC, relative percent) m/z = 202 (M^+, 100); UV (*n*-hexane) λ_{max} (log ϵ) = 216 (3.93) nm.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.21; H, 9.19.

6′,8′-Dimethylenespiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octan]-4′-one (63). The Swern oxidation[21] of dienol 61 was accomplished in the same way as the oxidation of dienol 40. Thus, 1.5 g of 61 (7.4 mmol) yielded 850 mg (57%) of 63 as a colorless liquid after purification by silica gel chromatography (pentane–ether (12/1)): R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.25; IR (CDCl$_3$) ν = 2984 (w), 2950 (s), 2860 (m), 1758 (vs), 1685 (m), 1665 (w), 1067 (w) cm^{-1}; ^{1}H-NMR (C_6D_6, 300 MHz) δ = 4.60 (1H, s), 4.59 (1H, s), 4.49 (1H, s), 4.47 (1H, s), 2.76–2.73 (1H, m), 2.66–2.62 (1H, m), 2.26–2.23 (1H, m), 2.13–2.09 (1H, m), 1.52–1.15 (8H, m); ^{13}C-NMR (C_6D_6, 75.47 MHz) δ = 202.36, 155.49, 149.04, 100.13, 98.60, 61.16, 56.85, 56.13, 54.11, 52.22, 34.55, 32.31, 25.65, 25.24; MS (DI, relative percent) m/z = 200 (M^+, 2); UV (*n*-hexane): λ_{max} (log ϵ) = 192 (4.25), 220 (3.77, sh), 300 (2.52) nm.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.02; H, 8.03.

6′,8′-Dimethylene-4′-methylspiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octan]-4′-ol (65). Methyllithium (9.4 mL of a 1.6 M solution in diethyl ether, 15 mmol) was added dropwise

to a magnetically stirred solution of spirodienone 63 (2.0 g, 10.0 mmol) in dry THF (100 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, poured into cold 2% aqueous HCl, and extracted with ether (2x). The combined organic layers were washed with 5% aqueous NaHCO$_3$ and brine, dried (MgSO$_4$), and evaporated. Purification of the residue by silica gel chromatography (elution with pentane–ether (12/1–9/1)) gave 65 (370 mg, 20%) as a colorless crystalline solid, which slowly decomposed in solution at rt: mp 72–73 °C (from pentane–ether (12/1) at –20 °C); R_f (SiO$_2$, pentane–ether (12/1), iodine) = 0.10; IR (CDCl$_3$) ν = 3604 (w), 2986 (m), 2946 (s), 2858 (m), 1665 (m), 1191 (m), 1181 (m), cm^{-1}; ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 4.43 (1H, s), 4.39 (1H, s), 4.36 (1H, s), 4.32 (1H, s), 2.92–2.88 (1H, m), 2.60–2.57 (1H, m), 2.50–2.47 (1H, m), 2.20–1.98 (3H, m), 1.7–1.2 (7H, m), 1.27 (3H, s); ^{13}C-NMR (CDCl$_3$, 75.47 MHz) δ = 156.94, 156.62, 94.96, 94.91, 82.78, 62.06, 58.53, 57.36, 57.15, 56.88, 38.20, 35.04, 27.46, 26.90, 24.20; MS (DI, relative percent) m/z = 216 (M^+, 1), 201 ($M^+ - CH_3$, 2), 125 (39), 105 (12), 92 (47), 91 (34), 79 (15), 77 (14), 67 (16), 65 (14), 43 (100), 41 (21) 39 (19); UV (*n*-hexane): λ_{max} (log ϵ) = 224 (3.77) nm.

4′,6′,8′-Trimethylenespiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octane] (67). A solution of methanesulfonyl chloride (235 mg, 2.1 mmol) in dry CH$_2$Cl$_2$ (20 mL) and a solution of triethylamine (1.5 mL, 11.2 mmol) in dry CH$_2$Cl$_2$ (40 mL) was added slowly and simultaneously to a magnetically stirred solution of dienol 65 (220 mg, 1.0 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h before being poured into cold 2% aqueous HCl. After extraction with ether (2x), the combined organic layers were washed with 5% aqueous NaHCO$_3$ and brine, dried (MgSO$_4$), and evaporated. Purification of the residue by silica gel chromatography (elution with pentane–ether (12/1)) afforded a fraction of several compounds (0.6 > R_f (SiO$_2$, pentane, iodine) > 0.3). Purification of this fraction by repeated silica gel chromatography (elution with *n*-pentane) at 0 °C gave 10 mg (5%) of 67 as a colorless liquid: R_f (SiO$_2$, pentane, iodine) = 0.34; ^{1}H-NMR (CD$_2$Cl$_2$, 300 MHz) δ = 4.53 (2H, s), 4.45 (2H, s), 4.32 (2H, s), 2.94 (2H, t, br, $J = 2.8$ Hz), 2.46 (2H, t, br, $J = 2.8$ Hz), 1.7–1.2 (8H, m).

4′,6′,8′-Triisopropylidenespiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octane] (68). endo-2-Isobutyryl-3-isopropylidenespiro[bicyclo[2.2.1]hept-5-ene-7,1′-cyclopentane] (58). A mixture of spiro[4.4]nona-2,5-diene (29)[18] (34.0 g, 0.28 mol) and allene 26[13–15] (36.0 g, 0.26 mol) was stirred at 50 °C for 4 d. Purification of the reaction mixture by silica gel chromatography (elution with pentane–ether (20/1–15/1)) gave 58 (24.0 g, 36%) as a colorless liquid with little impurities (mainly allene 26): R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.35; ^{1}H-NMR (C_6D_6, 300 MHz) δ = 6.10 (1H, dd, $J_1 = 5.7$ Hz, $J_2 = 3.0$ Hz), 5.69 (1H, dd, $J_1 = 5.7$ Hz, $J_2 = 2.7$ Hz), 3.52 (1H, s, br), 2.98 (1H, s, br), 2.50 (1H, s, br), 2.45 (1H, hept, $J = 6.9$ Hz), 1.66 (3H, d, $J = 1.0$ Hz), 1.51 (3H, s), 1.7–1.2 (8H, m), 1.00 (3H, d, $J = 6.9$ Hz), 0.99 (3H, d, $J = 6.9$ Hz); ^{13}C-NMR (C_6D_6, 75.47 MHz) δ = 210.14, 135.70, 133.77, 132.94, 123.93, 69.12, 56.58, 55.68, 55.18, 39.42, 32.39, 32.29, 26.13, 25.82, 23.16, 21.25, 19.93, 18.40.

4′-Oxa-5′-isopropyl-9′-isopropylidenespiro[cyclopentane-1,8′-tetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane] (60). A solution of 58 (8.0 g, 0.26 mol) in dry ether (2.5 L) was irradiated with a medium-pressure mercury lamp (Hanovia 450, $\lambda \geq 280$ nm) for 3 d. After removal of the solvent, the residue was chromatographed on silica gel (elution with CH$_2$Cl) to give 60 (3.4 g, 42%) as a colorless liquid: R_f (SiO$_2$, CH$_2$Cl$_2$, iodine) = 0.41; ^{1}H-NMR (C_6D_6, 300 MHz) δ = 4.62 (1H, dd, $J_1 = 3.5$ Hz, $J_2 = 2.2$ Hz), 3.00–2.95 (1H, m), 2.89–2.85 (1H, m), 2.38–2.34 (1H, m), 1.94–1.91 (1H, m), 1.80 (1H, hept, $J = 6.9$ Hz), 1.58 (3H, s), 1.50 (3H, s), 1.6–1.0 (8H, m), 1.11 (3H, d, $J = 6.9$ Hz), 1.07 (3H, d, $J = 6.9$ Hz); ^{13}C-NMR (C_6D_6, 75.47 MHz) δ = 144.75, 115.56, 101.75, 84.44, 62.56, 57.64, 57.07, 47.93, 47.29, 33.02, 31.59, 27.80, 25.36, 25.20, 20.22, 19.73, 18.87, 16.45.

6′,8′-Diisopropylidenespiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octan]-4′-ol (62). The cleavage of the oxetane ring of 60 induced by DATMP was accomplished in the same way as in the case of oxetane 39. Thus, 60 (10.3 g, 40 mmol) yielded 62 (5.9 g, 57%) as a colorless crystalline solid: mp 36–37 °C (from pentane–ether (9/1) at –20 °C); R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.07; IR (CDCl$_3$) ν = 3480 (m), 3010 (m), 2992 (m), 2940 (s), 2848 (s), 1442 (m), 1426 (m), 1282 (w), 1268 (w), 1248 (m),

1241 (m), 1176 (m), 1125 (w), 1111 (w), 1046 (s) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 4.38 (1H, dd, J_1 = 12.2 Hz, J_2 = 3.1 Hz), 3.06–3.05 (1H, m), 2.75–2.71 (1H, m), 2.39–2.36 (1H, m), 2.08 (1H, d, J = 12.2 Hz, OH), 2.05–2.02 (1H, m), 1.59 (3H, s), 1.57 (3H, s), 1.46 (3H, s), 1.44 (3H, s), 1.6–1.1 (8H, m); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 142.88, 141.40, 115.74, 109.80, 75.73, 59.26, 54.55, 53.18, 48.20, 43.08, 35.38, 35.10, 26.82, 25.83, 20.51, 20.18, 19.79, 19.44; MS (DI, relative percent) m/z = 258 (M$^+$, 5); UV (*n*-hexane) λ_{max} (log ϵ) = 216 (4.01) nm.

Anal. Calcd for C$_{18}$H$_{26}$O: C, 83.67; H, 10.14. Found: C, 83.81; H, 10.23.

6′,8′-Diisopropylidenespiro[cyclopentane-1,2′-tricyclo-[3.3.0.0^{3,7}]octan]-4′-one (64). The Swern oxidation[21] of spirodienol **62** was accomplished in the same way as the oxidation of dienol **40**. Thus, **62** (5.7 g, 22 mmol) yielded **64** (3.0 g, 53%) as a colorless crystalline solid: mp 43 °C (sealed tube, from pentane–ether (12/1) at –20 °C); R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.23; IR (CDCl$_3$) ν = 3018 (m), 2926 (s), 2908 (s), 1744 (vs), 1440 (m), 1181 (m), 1069 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.33–3.30 (1H, m), 2.92–2.88 (1H, m), 2.62–2.59 (1H, m), 2.13–2.10 (1H, m), 1.56 (3H, s), 1.51 (3H, s), 1.44 (3H, s), 1.43 (3H, s), 1.6–1.2 (8H, m); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 202.97, 141.08, 133.56, 117.20, 113.30, 60.06, 55.04, 53.70, 52.82, 45.19, 33.90, 32.17, 25.67, 25.39, 20.63, 20.10, 19.88, 19.67; MS (DI, relative percent) m/z = 256 (M$^+$, 10); UV (*n*-hexane) λ_{max} (log ϵ) = 202 (4.05), 298 (2.67), 308 (2.59, sh), nm.

Anal. Calcd for C$_{18}$H$_{24}$O: C, 84.33; H, 9.44. Found: C, 84.38; H, 9.49.

6′,8′-Diisopropylidene-4′-isopropylspiro[cyclopentane-1,2′-tricyclo[3.3.0.0^{3,7}]octan]-4′-ol (66). The reaction of dienone **64** with isopropyllithium was accomplished in the same way as in the case of dienone **41**. Thus, 1.5 g of **64** (5.8 mmol) afforded **66** (1.4 g, 80%) as a colorless crystalline solid: mp 69 °C (sealed tube, from pentane–ether (12/1) at –20 °C); R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.35; IR (CDCl$_3$) ν = 3606 (w), 2944 (s), 2848 (s), 1443 (w), 1258 (w), 1195 (m), 1177 (w), 1168 (w), 1005 (m) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 3.08 (1H, ddd, J_{1-3} = 3.1–3.0 Hz), 2.76 (1H, ddd, J_{1-3} = 2.9–2.8 Hz), 2.53 (1H, ddd, J_{1-3} = 3.0–2.9 Hz), 2.31 (1H, dd, br, J_1 = 13.6 Hz, J_2 = 6.8 Hz), 2.21–2.10 (1H, m), 1.89 (1H, ddd, J_{1-3} = 3.1–2.8 Hz), 1.83 (1H, hept, J = 6.7 Hz), 1.77–1.71 (1H, m), 1.63 (3H, s), 1.59 (3H, s), 1.57 (3H, s), 1.53 (3H, s), 1.6–1.2 (5H, m), 0.94 (1H, s), 0.91 (3H, d, J = 6.8 Hz), 0.82 (3H, d, J = 6.6 Hz); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 142.81, 140.69, 108.54, 107.68, 88.12, 58.03, 57.62, 55.08, 53.96, 50.56, 37.68, 35.75, 32.43, 27.66, 25.18, 21.34, 20.68, 19.57, 19.51, 17.96, 16.60; MS (DI, relative percent) m/z = 300 (M$^+$, 1); UV (*n*-hexane) λ_{max} (log ϵ) = 224 (4.02) nm.

Anal. Calcd for C$_{21}$H$_{32}$O: C, 83.94; H, 10.73. Found: C, 83.95; H, 10.82.

4′,6′,8′-Triisopropylidenespiro[cyclopentane-1,2′-tricyclo-[3.3.0.0^{3,7}]octane] (68). A solution of methanesulfonyl chloride (107 mg, 0.93 mmol) in dry CH$_2$Cl$_2$ (20 mL) and a solution of triethylamine (0.25 mL, 1.9 mmol) in dry CH$_2$Cl$_2$ (40 mL) was added slowly and simultaneously to a magnetically stirred solution of dienol **66** (140 mg, 0.47 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 19 h before being poured into cold 2% aqueous HCl. After extraction with ether (2x), the combined organic layers were washed with 5% aqueous NaHCO$_3$ and brine, dried (MgSO$_4$), and evaporated. Purification of the residue by silica gel chromatography (elution with pentane–ether (12/1)) afforded a fraction of several hydrocarbons (R_f (SiO$_2$, pentane–ether (9/1), iodine) = 0.66) and unreacted educt **66** (103 mg, 74%). Purification of the hydrocarbon fraction by silica gel chromatography (elution with *n*-pentane) at 10 °C gave **68** (3 mg, 2%) as a colorless oil: R_f (SiO$_2$, pentane, iodine) = 0.24; ^{1}H-NMR (C$_6$D$_6$, 200 MHz) δ = 3.33 (2H, t, br, J = 3 Hz), 2.58 (2H, t, br, J = 3 Hz), 1.70 (6H, s, br), 1.62 (6H, s), 1.56 (6H, s, br), 1.5–1.1 (8H, m); HR-MS (DI) m/z calcd (M$^+$) 228.1872, obsd 228.1837.

Determination of the Half-Lives of the trienes 9, 67, 37, and 68. A solution of 5–10 mg of triene 9, 37, or 68 (67) in 0.5 mL of C$_6$D$_6$ (CD$_2$Cl$_2$) (saturated with argon at room temperature) was heated at 30 °C (25 °C) in the NMR spectrometer. ^{1}H-NMR spectra were recorded in intervals of 10–20 min depending on the half-life of the triene. The signal areas of the olefinic protons of the educts which showed no overlap with signals of rearranged

products were turned to account relative to the signal area of the solvent. Analytical data of the rearranged trienes **13, 72,** and **45** were determined from these solutions. Attempts to isolate these triquinane derivatives failed due to polymerization which was observed after evaporation. **13:** R_f (SiO$_2$, pentane, iodine, UV) = 0.41; ^{1}H-NMR (C$_6$D$_6$, 300 MHz, 283 K): δ = 5.69 (1H, s, br), 5.06–5.04 (1H, m), 4.90 (1H, s, br), 4.77 (1H, s, br), 3.55 (1H, s, br), 3.22–3.08 (2H, m), 2.38–2.13 (5H, m). **72:** ^{1}H-NMR (CD$_2$Cl$_2$, 300 MHz) δ = 5.66–5.63 (1H, m), 5.00–4.98 (1H, m), 4.93 (1H, s, br), 4.57 (1H, s, br), 3.78 (1H, d, br, J = 5.8 Hz), 2.82 (1H, dm, br, J = 5.8 Hz), 2.75–2.36 (4H, m), 1.82–1.24 (8H, m). **45:** R_f (SiO$_2$, pentane, iodine, UV) = 0.35; ^{1}H-NMR (C$_6$D$_6$, 200 MHz) δ = 5.90 (1H, d, J = 1.7 Hz), 5.05–5.01 (1H, m), 3.98 (1H, d, br), 3.38–3.04 (2H, m), 2.36 (1H, d, br, J = 16 Hz), 1.71 (3H, s, br), 1.67 (3H, s, br), 1.14 (3H, s), 1.11 (3H, s), 1.06 (3H, s), 1.04 (3H, s).

Thermolysis of the Dienones 35, 41, 63, and 64. For determination of the half-lives, solutions of 25 mg of dienone (**35, 41, 63,** or **64**) in 0.5 mL of C$_6$D$_6$ (saturated with argon) were heated at 50 °C in the NMR spectrometer. ^{1}H-NMR spectra were recorded in intervals of 5–15 min depending on the half-life of the dienone. The areas of educt signals (6.0 < δ < 2.5), which showed no overlap with signals of rearranged products, were turned to account relative to the signal area of the solvent. After thermolysis of the dienones, the rearranged products were purified by silica gel chromatography (elution with pentane–ether mixtures). Thermolysis of **35** yielded **36** as a colorless oil: bp 60 °C (3 mm) (Kugelrohr); IR (GC) ν = 2970 (w), 2935 (w), 1728 (vs), 1620 (w), 1130 (w) cm^{-1}; ^{1}H-NMR (CDCl$_3$, 200 MHz) δ = 5.74–5.72 (1H, m), 5.09–5.07 (1H, m), 3.71 (1H, s, br), 3.12–2.68 (5H, m), 2.56–2.37 (2H, m); ^{13}C-NMR (CDCl$_3$, 50.32 MHz) δ = 212.54, 186.74, 144.81, 125.24, 120.16, 61.79, 46.23, 38.74, 29.32, 26.43; MS (GC, relative percent) m/z = 146 (M$^+$, 66).

Thermolysis of **41** at 50 °C afforded a mixture of **42** and **43** (ratio 1/1, ^{1}H-NMR). Purification as described above yielded **42** as a colorless crystalline solid and **43** as a colorless oil. **42:** mp 92 °C (sealed tube); R_f (SiO$_2$, pentane–ether (1/1), iodine) = 0.42; IR (CDCl$_3$) ν = 2980 (m), 2956 (s), 2920 (m), 2864 (w), 2848 (w), 1685 (vs), 1596 (s), 1317 (w), 1191 (w), 1139 (m), 1129 (w), 841 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 200 MHz) δ = 5.60 (1H, d, J = 1.6 Hz), 4.69–4.65 (1H, m), 3.45–3.40 (1H, m), 2.84 (1H, ddm, J_1 = 16.4 Hz, J_2 = 10.0 Hz), 2.73 (1H, ddd, J_1 = 10.1 Hz, J_2 = 5.3 Hz, J_3 = 1.0 Hz), 2.47 (1H, dm, J = 16 Hz), 0.93 (3H, s), 0.91 (3H, s), 0.81 (3H, s), 0.78 (3H, s); ^{13}C-NMR (C$_6$D$_6$, 50.32 MHz) δ = 210.81, 193.92, 156.08, 122.85, 116.77, 58.76, 48.31, 47.81, 46.39, 39.65, 24.45, 24.35, 23.48, 23.45; MS (DI) m/z = 202 (M$^+$, 72); UV (*n*-hexane): λ_{max} (log ϵ) = 204 (4.06), 220 (3.94, sh), 262 (3.51), 324 (1.76) nm.

Anal. Calcd for C$_{14}$H$_{18}$O: C, 83.12; H, 8.97. Found: C, 83.15; H, 9.02.

43: mixture of s-trans (**43a**) and s–cis (**43b**) isomers.

43a: R_f (SiO$_2$, pentane–ether (1/1), iodine, UV) = 0.61; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 6.25 (1H, s, br), 4.92 (1H, s, br), 4.88 (1H, s, br), 3.5–3.0 (2H, overlap of signals), 2.08 (3H, s), 1.79 (3H, s), 1.65 (3H, s), 2.2–1.2 (3H (?), m, overlap of signals), 0.75–0.95 (1H (?), m); ^{13}C-NMR (CDCl$_3$, 50.32 MHz) δ = 217.51, 147.56, 138.44, 136.23, 128.44, 127.66, 113.49, 53.48, 45.67, 36.21, 25.44, 22.41, 21.44, 21.08; MS (GC, relative percent) m/z = 203 (M$^+$ + 1, 16), 202 (M$^+$, 100), 160 (M, 40), 159 (53), 147 (18), 146 (58), 145 (48), 131 (57), 129 (18), 128 (18), 117 (19), 116 (15), 115 (31), 105 (23), 91 (43), 77 (22), 65 (12), 51 (13), 41 (21), 39 (24).

43b: R_f (SiO$_2$, pentane–ether (1/1), iodine, UV) = 0.61; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 6.32 (1H, d, J = 1.4 Hz), 6.01 (1H, s, br), 5.22 (1H, s, br), 3.5–3.0 (2H, overlap of signals), 1.84 (3H, s), 1.64 (3H, s), 1.53 (3H, s), 2.2–1.2 (3H (?), m, overlap of signals), 0.75–0.95 (1H (?), m); ^{13}C-NMR (CDCl$_3$, 50.33 MHz) δ = 216.51, 143.30, 143.01, 137.70, 125.51, 129.27, 116.69, 57.24, 42.34, 36.05, 27.15, 21.34, 21.30, 21.20; MS (GC) m/z = 203 (M$^+$ + 1, 10), 202 (M$^+$, 67), 160 (M, 24), 159 (39), 147 (18), 146 (100), 131 (58), 129 (17), 128 (17), 117 (15), 116 (15), 115 (30), 105 (19), 91 (43), 77 (21), 65 (12), 51 (13), 41 (21), 39 (25). The assignment of the NMR signals of **43a** and **43b** could be made, as the ratio of both compounds after thermolysis of **41** was different from the ratio after chromatography (^{1}H-NMR).

Thermolysis of **63** afforded **71** as a colorless liquid: R_f (SiO$_2$, pentane–ether (9/1), iodine, UV) = 0.09; IR (film) ν = 2948 (s),

2864 (m), 1685 (vs), 1611 (s), 1155 (w), 845 (m) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 300 MHz) δ = 5.57 (1H, s, br), 4.75 (1H, s, br), 3.18 (1H, d, br, J = 5.1 Hz), 2.45 (1H, d, J = 5.2 Hz), 2.3–1.9 (6H, m), 1.7–1.5 (5H, m), 1.35–1.2 (1H, m); ^{13}C-NMR (C$_6$D$_6$, 75.47 MHz) δ = 209.02, 185.09, 144.33, 129.74, 126.18, 64.38, 62.02, 57.96, 42.87, 34.37, 30.10, 27.00, 24.31, 23.74; MS (DI) m/z = 200 (M$^+$, 100), 172 (42), 171 (80), 158 (38), 157 (40), 143 (30), 129 (82), 128 (83), 115 (83), 91 (78), 77 (57), 65 (50), 63 (33), 51 (54), 41 (48) 39 (100); UV (n-hexane) λ_{max} (log ϵ) = 202 (4.05), 260 (3.38), 330 (2.46) nm.

Thermolysis of **64** at 50 °C afforded dienone **69** and trienone **70** (ratio 4/1, ^{1}H-NMR). Purification as described above yielded **69** as a colorless crystalline solid and a mixture of **70** (s-trans isomer) and **70b** (s-cis isomer) (ratio 4/1, ^{1}H-NMR) as a colorless oil: **69**: mp 95 °C (from pentane at –20 °C); R_f (SiO$_2$, pentane–ether (9/1), iodine, UV) = 0.09; IR (CDCl$_3$) ν = 2954 (s), 2866 (m), 1679 (vs), 1599 (s), 1185 (w), 1155 (w), 1134 (w) cm^{-1}; ^{1}H-NMR (C$_6$D$_6$, 200 MHz) δ = 5.58 (1H, d, J = 1.5 Hz), 4.76 (1H, d, J = 2.0 Hz), 3.54 (1H, dm, J = 5.2 Hz), 2.51 (1H, d, J = 5.2 Hz), 2.18–2.09 (2H, m), 1.69–1.57 (4H, m), 1.35–1.27 (2H, m), 0.96 (3H, s), 0.91 (3H, s), 0.87 (3H, s), 0.81 (3H, s); ^{13}C-NMR (C$_6$D$_6$, 50.33 MHz) δ = 209.07, 193.43, 154.34, 125.54, 122.62, 63.91, 58.43, 58.33, 48.26, 45.83, 43.09, 34.49, 24.58, 24.44, 24.41, 23.77, 23.65, 23.47; MS (DI, relative percent) m/z = 256 (M$^+$, 30); UV (n-hexane) λ_{max} (log ϵ) = 204 (4.08), 218 (3.93, sh), 264 (3.38), 330 (1.47) nm.

Anal. Calcd for C$_{18}$H$_{24}$O: C, 84.33; H, 9.44. Found: C, 84.26; H, 9.19.

Analytical data of **70** from mixtures with **64**, **69**, and **70b**. **70**: R_f (SiO$_2$, pentane–ether (9/1), iodine, UV) = 0.26; ^{1}H-NMR (C$_6$D$_6$, 200 MHz) δ = 6.37 (1H, d, J = 2.0 Hz), 6.04 (1H, s, br), 5.20 (1H, s, br), 3.64 (1H, d, br, J = 7 Hz), 3.11 (1H, d, br, J = 7 Hz), 2.19 (1H, d, J = 15.8 Hz), 1.85 (3H, s), 1.77 (1H, dd, J_1 = 15.8 Hz, J_2 = 1.2 Hz), 1.66 (3H, s), 1.58 (3H, s), 1.6–0.9 (8H, m); ^{13}C-NMR (C$_6$D$_6$, 50.33 MHz) δ = 212.56, 144.50, 140.90, 137.96, 129.74, 126.11, 117.36, 59.79, 51.21, 49.99, 49.70, 40.79, 34.58, 24.11, 23.66, 23.11, 21.40, 21.06, 23.47.

Supplementary Material Available: NMR spectra of compounds 9, 13, 35–37, 42, 43, 67, 68, and 70–72 (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page ordering information.