Synthesis and Reactions of Novel Tricyclo[4.3.1.1^{2,5}]undec-3-en-10-ones

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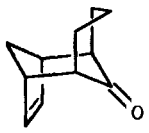
Sodium iodide/copper mediated intermolecular cyclodehalogenation of 2,6-dibromocyclohexanones in the presence of furan and cyclopentadiene afforded a variety of alkylated tricyclo[4.3.1.1^{2,5}]undec-3-en-10-ones. An alkyl group (methyl or isopropyl) adjacent to the carbonyl carbon atom in the starting 2,6-dibromocyclohexanone derivative was important for the success of the cycloaddition procedure. Even tricyclic ketone **11**, containing two quaternary carbon atoms adjacent to the carbonyl carbon atom, was prepared. The α,α'-dibromoketones derived from either enantiomer of menthone and cyclopentadiene reacted enantioselectively, yielding tricycles (7*R*)-**7** and (7*S*)-**7**. Since a number of tricyclic ketones **3**–**11** were sensitive, they were reduced to secondary alcohols **19**–**25**, having an axial, α-configurated OH group and were also converted into tertiary methylcarbinols **26** and **27** using methyllithium activated with *t*BuOK. Secondary α-configurated alcohols **19**–**25** had an earthy-mouldy odour, and tertiary carbinols **26** and **27** even more so. Unsaturated alcohols **26** and **27** showed a ^4J coupling of 2 Hz between the rigidly held OH proton and the nearest methyl protons. On hydrogenation of the olefinic double bond (**4** → **33**, **11** → **34**) this long-range coupling disappeared.

We have recently described diastereoface-selective cycloadditions of metal oxidoallyl cations to pinofurans, i.e. chiral fused 1,3-dienes, which were prepared from enantiomerically pure nopol via β-pinene[1]. In continuation of this work, we now report on oxyallyl cation cycloadditions to alkylated 2,6-dibromocyclohexanones, which give rise to various tricyclo[4.3.1.1^{2,5}]undec-3-en-5-ones. While both the parent tricycle **1**[2,3] and its 11-oxa derivative **2**[2,4,5] are known, there has been, as yet, no work on derivatives of **1** and **2**. Alkylated tricycles, containing the skeleton of **1** and **2**, can exist as diastereomers and enantiomers.



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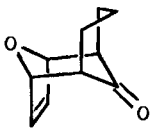

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Results

We began with model experiments using simple 2,6-dibromocyclohexanone (**12**). As we have shown several times, it is essential in cycloadditions of oxyallyl cations that the metal oxidoallyl cation generated has correctly matched electrophilicity and nucleophilicity for its reaction partner, i.e. the conjugated diene[6]. As it turned out, the sodium iodide/copper mediated cyclodehalogenation of α,α'-dibromo ketones[7,8], which we introduced some time ago[7], did not work well for **12** and furan; the known 11-oxatricycle **2** was obtained in only 10% yield. However, the simple structural change from **12** to 2,6-dibromo-2-methylcyclohexanone (**13**) gave cycloadducts **3** and **4** in acceptable yields, after a number of procedural improvements had been made (see below and Experimental). Even the crowded adducts **5** could now be isolated from the reaction of **14** and *cyclopentadiene*. However, **14** and *furan* reacted to give **14a**, i.e. a product of class C[6] or electrophilic substitution. Cycloadducts **10** and **11** which have *two* sterically demanding quaternary carbon centres each, were obtained from the reaction of **17** with furan and cyclopentadiene, respectively. Attempted cycloadditions with the overcrowded dibromo ketone **18** failed.

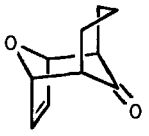
For comparison the zinc/triethyl borate method[9] was tried, but with mixed success. In the case of tricycle **6** the yield was improved from 22 to 35% (Scheme 1). With the ditertiary dibromo ketone **17** we obtained 1,4-diketone **17a** by reductive dimerization.

Menthone (**15a**) and carvomenthone (**16a**) are two naturally occurring monoterpenes, of which either enantiomer is available optically pure. On preparation of **15** from **15a** and of **16** from **16a**, racemization ensues at the tertiary carbon atom vicinal to the carbonyl carbon atom. However, the remote, starred carbon atoms in **15**/**15a** and **16**/**16a** are not affected by dibromination. Thus, the reaction of the dibromo ketone from (−)-menthone and cyclopentadiene gave tricycle (7*R*)-**7**, which was the enantiomer of the cycloadduct obtained from the dibromo ketone of (+)-menthone (see below).

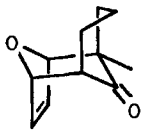
The methyl group at C-7 in tricycles **6**/**7** is seen to adopt the least crowded *exo* position with respect to the [3.2.1] skeleton. This assignment was supported by an X-ray crystal-structure determination of secondary alcohol **31** (Figure

  0009–2940/90/1111–2131 $ 3.50+.25/0

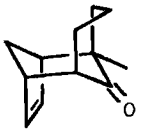
Scheme 1. Tricyclo[4.3.1.1^{2,5}]undec-3-en-10-ones prepared by the NaI/Cu procedure [isolated yields after chromatography]



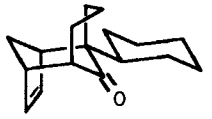
2 [9.5%]



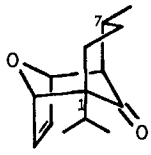
3 [25(15^{a})%]



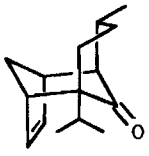
4 [20 - 25%]



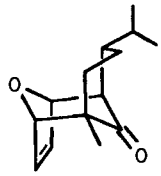
5 [10 - 13%]



6 [22(35^{a})%]

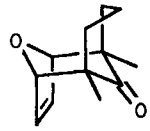


7 [25 - 30(5^{a})%]

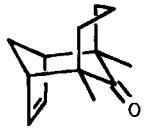


8 [27%]

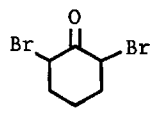
9 [30 - 41%]



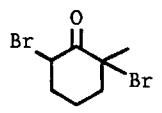
10 [14 - 22%]



11 [6 - 18%]



12



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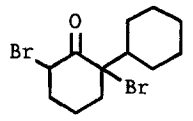

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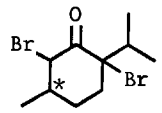

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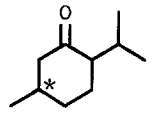
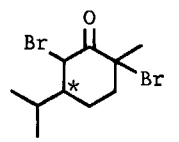


15a



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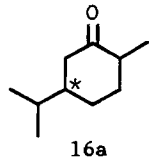
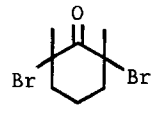
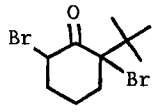


16a



17



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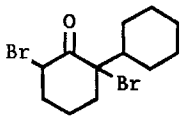

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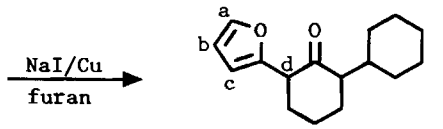
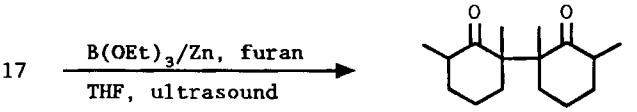
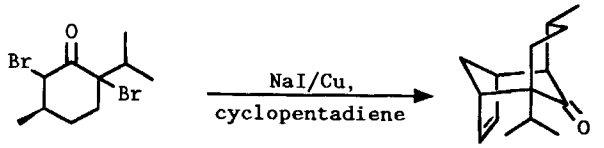


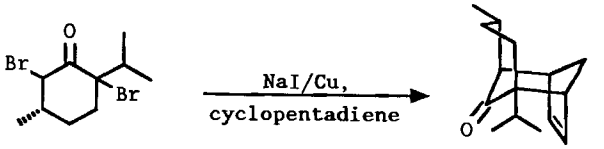
14a



17a (32%);
cf. ref.[22]



(5R)-15 → (7R)-7 (25 - 30%)



(5S)-15 → (7S)-7 (25 - 30%)

[a] Yields for preparations by the $B(OEt)_3$/Zn method[9].

1), which was obtained by reduction of ketone **6** (see below). The structure of supposedly rigid tricycle **31** is of interest, because C8 has an unusually high anisotropic thermal ellipsoid (Figure 1b). The difference Fourier synthesis near this atom (all atoms subtracted, but C8) shows an ellipsoidal electron density distribution without suggesting any two-site occupancy. Hence the high thermal anisotropy for C8 could not be separated in two alternate site occupancies. However, the *exo* position of the C16 methyl group is secure (Figure 1a,b), and the isopropyl group in **8** and **9** can be assumed to have *exo* configuration, also.

The various unsaturated tricycles, especially those derived from cyclopentadiene, are sensitive compounds. Both reaction conditions (4–6 h reaction time at room temp.) and workup, carried out under external cooling with ice and, preferably, under N_2, had to be mild. The crude product was a yellow oil. If workup was delayed or carried out incorrectly, the product turned brown, with a drop in yield and

complications during flash chromatography. A further trick was developed for cycloadditions with cyclopentadiene: It was found advantageous to precool the cyclopentadiene to −78 °C and to add it slowly by syringe to the reaction mixture, synchronously with the α,α′-dibromo ketone which was added with another syringe. In this fashion, dimerization of cyclopentadiene was suppressed, workup was simplified, and the yields of cycloadducts were increased. Using this procedural improvement for cycloadduct **11**, the yield increased threefold, from 6 to 18%. On being kept in the refrigerator, the cyclopentadiene adducts turned dark, whereas furan adducts appeared to be more stable.

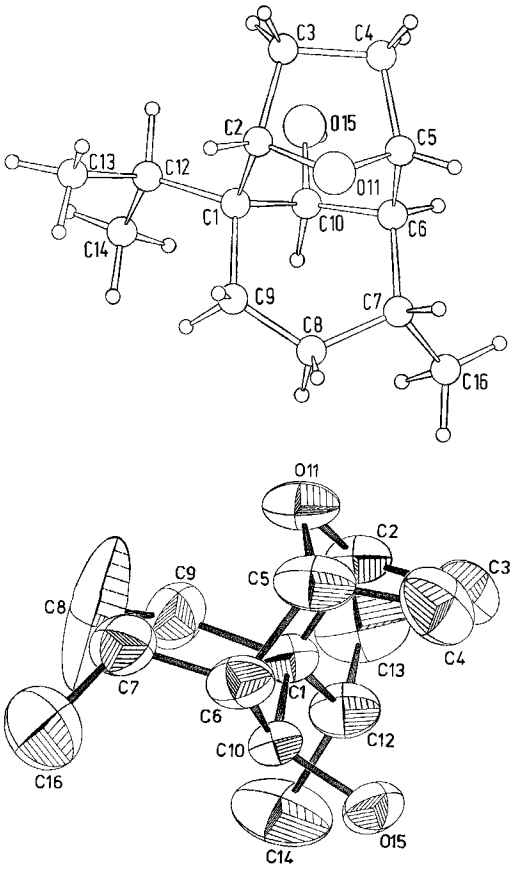


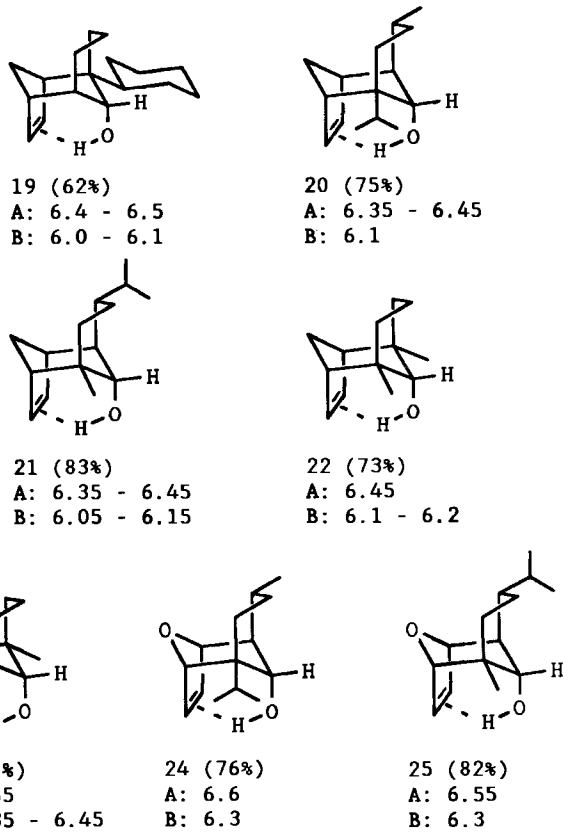
Figure 1. X-ray crystal structure of **31** (top: SCHAKAL; bottom: ORTEP)

For this reason, the tricycles were reduced to the more stable secondary alcohols, which could be stored for a longer time and could also be readily chromatographed.

Reduction with $LiAlH_4$

Initial attemps to reduce the ketone carbonyl group with $NaBH_4$ were not successful. Apparently, the carbonyl carbon atom is highly hindered; on TLC plates the compounds did not react with 2,4-dinitrophenylhydrazine, either. $LiAlH_4$ was successful and gave the *endo*-alcohol. However, longer reaction times gave overreduction, with disappearence of the olefinic double bond. The α configuration of the OH group was determined by spectroscopic criteria established previously by us[10] and corroborated by others[11,12]. Thus, the signals of the olefinic protons in the alcohols **19**–**25** appeared downfield from those of the precursor ketones (Scheme 2), consistent with intramolecular hydrogen bonding. The ^{13}C-NMR signals of the olefinic carbon atoms in the alcohols also appeared downfield from the corresponding signals of the precursor ketones.

Scheme 2. Tricyclo[4.3.1.1^{2,5}]undec-3-en-10-ols from $LiAlH_4$ reduction of the ketones (isolated yields); δ values of the signals of the olefinic protons of the alcohol (A) and the ketone precursor (B)



All alcohols had an earthy-mouldy[11a] odour except for **19** (molecular weight 246), which was almost odourless. In a recent paper, Rouessac et al. have suggested[13], drawing on work of Polak[14], Mookherjee[15], and Brunke[16], that the following structural criteria are necessary for an earthy odour: (i) a rigid bicyclic or tricyclic structure with 10–15 carbon atoms, (ii) an axial or semiaxial tertiary OH group, (iii) a methyl or geminal dimethyl grouping adjacent to the carbinol carbon atom.

It is of interest that these structural criteria are fulfilled for the alcohols **20**–**25**, except that they are *secondary* and not tertiary. However, a series of related tertiary alcohols showed an even stronger earthy smell (see below).

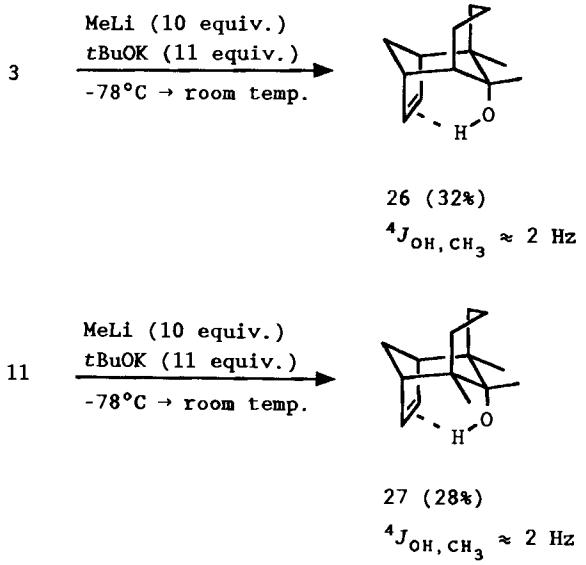
The two alcohols (7*R*)-**20** and (7*S*)-**20** prepared from ketones (7*R*)-**7** and (7*S*)-**7**, respectively, showed identical ^{1}H- and ^{13}C-NMR, IR, and mass spectra. They also had the same mp (64 °C). The optical rotations were $[\alpha]_D^{20}$ −48.8 and

$[\alpha]_D^{25}$ = 42.6, respectively. The optical rotations of the derived hydrogenated alcohols were equal and opposite $\{[\alpha]_D^{25}$ = 10.69 for (7*R*)-**29** and −10.85 for (7*S*)-**29**$\}$.

Preparation of Tertiary Alcohols

In order to probe structure-odour relationships further, we converted tricyclic ketones **3** and **11** into their tertiary methylcarbinols. The conversion succeeded under conditions previously developed by Giesel in our group[17]. The chemical shift of the signals of the olefinic protons in **26** and **27** was δ = 6.55, i.e. even further downfield than in the secondary alcohol **22** (δ = 6.45) (Scheme 3).

Scheme 3

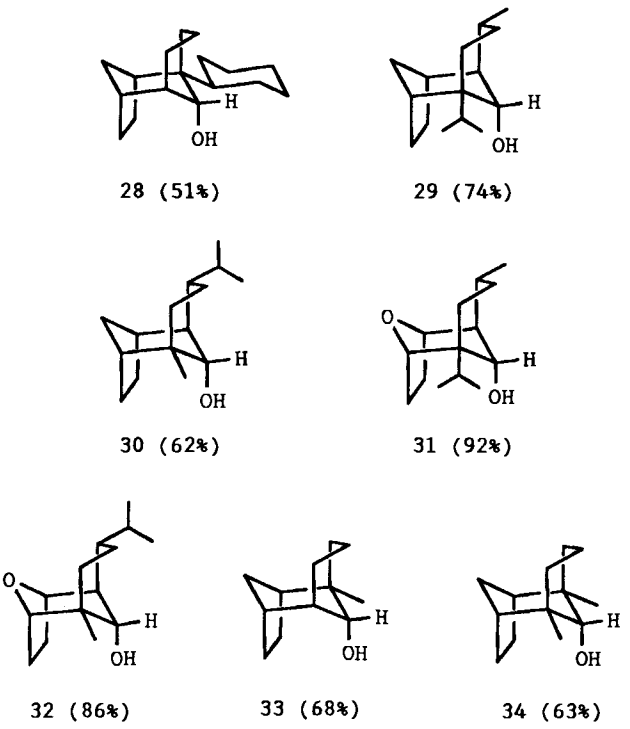


It is interesting that the OH proton in **26** and **27** coupled with the protons of the newly introduced methyl group (^4J = 2 Hz). NMR and IR evidence showed that the OH group in **26** and **27** is held rigidly by intramolecular hydrogen bonding. On hydrogenation of the double bond in **26** and **27**, the ^4J coupling disappeared. Therefore, we suggest that the rigidly held OH group in **26** and **27**, which is also antiperiplanar to the coupling methyl group, contributes to the unusual long-range coupling. Both **26** and **27** had a very strong earthy odour, **27** more than **26** and both stronger than the secondary alcohols in Scheme 2.

The catalytic hydrogenation of the double bond of secondary alcohols (cf. Scheme 2) and of tertiary alcohols **26**, **27** was generally straightforward, although a number of secondary alcohols decomposed. The resulting saturated alcohols are listed in Scheme 4. On evaporation of the solvent after chromatography, all alcohols, as far as they were crystalline, tended to grow out of solution onto the glass walls of the vessel. The tertiary alcohols **33** and **34** had a strong earthy odour.

In summary, a series of rigid tricyclic unsaturated ketones and their derivatives have been prepared for the first time. Key intermediates were cyclic allylic cations, which were generated from naturally occurring terpenoid dibromo ketones with defined configuration. The tricycles have interesting physical and spectroscopic properties, and they are of olfactory interest.

Scheme 4. Saturated alcohols **28**–**34** (isolated yields)



We thank Dr. *D. J. Williams* for a discussion of the X-ray data and the *Fonds der Chemischen Industrie* for support of our work.

Experimental

Column chromatography (silica gel, 0.02–0.063 mm, Merck) was carried out under weak positive pressure. – TLC: Precoated plates, Macherey-Nagel, Merck. – Gas chromatography: FID, N_2, Varian A 1400. Glass capillary column (25 m, type OV 1 CB) and SE 54 CB (25 m fused silica, widebore). – Melting points: Büchi apparatus. – Optical rotations: Perkin-Elmer polarimeter 241. – IR: Electrophotometer 580 and FT spectrometer 1710, Perkin-Elmer. – ^{1}H NMR: WP 80, WH 90, WP 200 SY and AM 300, Bruker. – ^{13}C NMR: WP 200 SY, AM 300, Bruker. – MS: Spectrometer MAT 312, Finnigan. – Elementary analyses: Microanalytical laboratory of the Department of Organic Chemistry.

α,α′-Dibromo ketones **12**[18], **13**[18], **15**[19], **16**[20], **17**[21], and **18**[18] were prepared as described. In the tricycles, proton 11-H_a is *anti* to the olefinic double bond, 11-H_b is *syn*.

2,6-Dibromo-2-cyclohexylcyclohexanone (**14**): Bromine (32 g, 0.2 mol) was added dropwise to a solution of 2-cyclohexylcyclohexanone (9.0 g, 50 mmol) in CCl_4 (50 ml). The mixture was stirred at room temp. for ca. 1 h, the HBr formed was removed with an aspirator, and the residue was poured onto ice (100 g) and stirred for 5 min. The organic phase was separated, washed with satd. aqueous $NaHCO_3$ (4 × 50 ml), water (50 ml), and dried ($MgSO_4$). The organic solvent was evaporated (the temp. should not exceed 20°C, and the product should not be exposed to direct sunlight), giving a brown oil, which was recrystallized from methanol (50 ml) [yield 12 g (70%)] and used directly in the next stage. – IR ($CHCl_3$): $\tilde{\nu}$ = 2940 cm^{-1}, 2860, 1725, 1450. – ^{1}H NMR ($CDCl_3$):

δ = 0.95–2.70 (m, 17H), 5.50 (dd, *J* = 6 Hz, *J* = 12 Hz, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 22.8 (t), 26.4 (2 t), 26.6 (t), 29.0 (t), 29.1 (t), 35.8 (t), 38.2 (t), 45.5 (d, C-7), 52.7 (d, C-6), 77.1 (s, C-2), 194.6 (s, C-1). – MS (70 eV, 40°C): *m/z* (%) = 340 (1) [M^+], 338 (1.7), 336 (1), 259 (27), 258 (50), 256 (100), 254 (52), 257 (29).

Zinc/Triethyl Borate Method[9]. – *Illustrative Procedure for the Preparation of* **6**: Powdered zinc (0.46 g, 7.0 mmol) and furan (1.02 g, 15 mmol) were placed into a flame-dried flask filled with N_2 (balloon) and equipped with a reflux condenser. The flask was suspended in a water-filled sonicator (Brasonic 220) (ca. 10°C), and the zinc was preactivated by sonication. The dibromo ketone **15** (1.56 g, 5.0 mmol) and triethyl borate (1.46 g, 10 mmol) in anhydrous THF (5 ml) were slowly added over 20 min. After the mixture had been sonicated for 5 h, water (2 ml) was added, and the resulting precipitate was dissolved with satd. aqueous NH_4Cl (15 ml). The mixture was extracted with ether (4 × 10 ml), the organic phase was washed with aqueous $NaHCO_3$ (2 × 10 ml) and NaCl (10 ml), dried ($MgSO_4$), and freed from solvent (rotary evaporator). The resulting crude yellow oil was chromatographed [silica gel, petroleum ether/ether (3:1)] to give **6**; 0.39 g (35%), m.p. 83°C, $[\alpha]_D^{23}$ = +10.99 (*c* = 1.31 in CH_2Cl_2). – IR ($CHCl_3$): $\tilde{\nu}$ = 2970 cm^{-1}, 2940, 2880, 1710. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (d, *J* = 7 Hz, 3H, CH_3), 1.00 (t, *J* = 7 Hz, 6H, isopropyl-CH_3), 1.0–2.7 (m, 7H), 4.70 (s, 1H, 2-H), 4.80 (dd, *J* = 1 Hz, *J* = 2 Hz, 1H, 5-H), 6.30 (t, *J* = 1 Hz, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 17.3 (q, isopropyl-CH_3), 18.4 (q, isopropyl-CH_3), 22.9 (q, CH_3), 28.2 (d, C-7), 28.7 (t, C-8), 30.9 (t, C-9), 36.1 (d, isopropyl-CH), 59.7 (s, C-1), 59.8 (d, C-6), 83.1 (d, C-5), 84.8 (d, C-2), 133.9 (d, C-3), 134.8 (d, C-4), 212.5 (s, C-10). – MS (70 eV): *m/z* (%) = 220 (94) [M^+], 205 (85), 177 (52), 176 (81), 163 (37), 152 (31), 149 (44), 137 (46), 108 (100).

$C_{14}H_{20}O_2$ (220.1) Calcd. C 76.33 H 9.15 Found C 76.00 H 9.10
Calcd. 220.1463 Found 220.1463 (MS)

1,1',3,3'-Tetramethylbicyclohexyl-2,2'-dione (**17a**): Dibromo ketone **17** (0.45 g, 1.6 mmol), zinc powder (0.13 g, 2.0 mmol), furan (0.41 g, 6.0 mmol) and triethyl borate (0.47 g, 3.2 mmol) in dry THF (3.5 ml) were allowed to react as detailed for **6**. Reductive dimerization[22] and column chromatography afforded **17a** (0.06 g, 32%), colorless liquid. – IR ($CHCl_3$): $\tilde{\nu}$ = 2970 cm^{-1}, 2930, 2830, 1690, 1450, 1380, 1370, 1130, 1115, 990. – ^{1}H NMR ($CDCl_3$): δ = 1.3 (d, *J* = 7 Hz, 6H, 2 CH_3), 1.4 (s, 3H, CH_3), 1.7 (s, 3H, CH_3), 1.5–2.0 (m, 12H, 6 CH_2), 2.35–2.60 (m, 2H, methine-H). – ^{13}C NMR ($CDCl_3$): δ = 15.5 (q), 19.0 (q), 22.2 (q), 34.2 (t), 36.4 (t), 42.4 (d, C-3), 52.8 (s, C-1), 216.2 (s, C-2). – MS (70 eV): *m/z* (%) = 250 (16) [M^+], 179 (13), 165 (9), 153 (19), 135 (12), 126 (100), 109 (13), 95 (14), 81 (15), 67 (16).

$C_{16}H_{24}O_2$ Calcd. 250.1932 Found 250.1933 (MS)

General Procedure for the NaI/Cu Method: A mixture of anhydrous NaI (9.00 g, 60 mmol) and copper powder (1.90 g, 30 mmol) in acetonitrile (20 ml) was stirred vigorously under N_2, whilst cyclopentadiene (1.65 g, 25 mmol) (which had been cooled to –78°C) and the α,α'-dibromo ketone (10 mmol) in acetonitrile (20 ml) were added dropwise synchronously and separately with two syringes over 1 h (unlike cyclopentadiene, furan was added in a single portion). The mixture was stirred for 6 h at room temp., poured onto water (50 ml) and ice (50 g), and stirred until the ice had just melted. During workup the temperature should not rise above 5°C, and contact with oxygen should be avoided (otherwise the product may turn brown). The mixture was filtered through silica gel, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (4 × 10 ml). The combined organic phases were washed with ice-cold concd. NH_3 (ca. 7 × 20-ml portions) until the blue color of copper(II) had practically disappeared, washed with water (3 × 15 ml), dried (Na_2SO_4), and freed from solvent. The resulting light yellow product was purified by chromatography [silica gel, ethyl acetate/light petroleum ether (1:12)].

11-Oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-one (**2**): 2,6-Dibromocyclohexanone (1.28 g, 5.0 mmol) and furan (1.36 g, 20 mmol) were allowed to react, giving **2**; 0.08 g (9.5%), colorless oil. IR, ^{1}H-NMR, and mass spectra have been described[2,3]. – ^{13}C NMR ($CDCl_3$): δ = 20.9 (t, C-8), 31.1 (t, C-7, C-9), 53.2 (d, C-1, C-6), 83.6 (d, C-2, C-5), 135.5 (d, C-3, C-4), 215.2 (s, C-10).

1-Methyl-11-oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-one (**3**): 2,6-Dibromo-2-methylcyclohexanone (1.35 g, 5.0 mmol) and furan (1.36 g, 20 mmol) were allowed to react according to the general procedure, giving **3**; 0.22 g (25%), fine platelets, m.p. 54°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2980 cm^{-1}, 2840, 1715, 1500, 1435, 1370, 1310, 1105, 1080, 935, 900. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (s, 3H, CH_3), 1.4–2.7 (m, 7H), 4.60 (s, 1H, 2-H), 4.95 (d, *J* = 2 Hz, 1H, 5-H), 6.40 (s, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 18.3 (q, CH_3), 21.2 (t, C-8), 30.9 (t, C-7), 40.3 (t, C-9), 52.1 (d, C-6), 54.0 (s, C-1), 83.9 (d, C-5), 87.4 (d, C-2), 135.0 (d, C-4), 136.3 (d, C-3), 214.9 (s, C-10). – MS (70 eV): *m/z* (%) = 178 (85) [M^+], 163 (74), 150 (28), 135 (87), 121 (47), 110 (100), 95 (82), 79 (66), 67 (77), 55 (70).

$C_{11}H_{14}O_2$ Calcd. 178.0994 Found 178.0994 (MS)

1-Methyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-one (**4**): 2,6-Dibromo-2-methylcyclohexanone (1.35 g, 5.00 mmol) and cyclopentadiene (0.83 g, 12.6 mmol) were allowed to react according to the general procedure, giving **4**; 0.22 g (25%), yellow oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 2950 cm^{-1}, 2880, 1710, 1455, 1375, 1340. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (s, 3H, CH_3), 2.3–2.4 (m, 6H), 2.40–2.50 (m, 2H, CH, 11-H_b), 2.75 (d, ^2J = 11 Hz, 1H, 11-H_a), 2.70–2.80 (m, 2H, CH), 6.05–6.15 (m, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 19.5 (d, C-8), 23.3 (q, CH_3), 28.6 (t, C-7), 36.8 (t), 38.5 (t), 46.2 (d), 48.5 (d), 49.9 (s, C-1), 52.4 (d, C-2), 137.0 (d, C-3), 139.4 (d, C-4), 218.8 (s, C-10). – MS (70 eV): *m/z* (%) = 176 (22) [M^+], 151 (4.7), 133 (15), 111 (100), 110 (54).

$C_{12}H_{16}O$ Calcd. 176.1201 Found 176.1202 (MS)

1-Cyclohexyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-one (**5**): According to the general procedure, 2,6-dibromo-2-cyclohexylcyclohexanone (3.40 g, 10 mmol) and cyclopentadiene (1.65 g, 25 mmol) were allowed to react, giving **5**; 0.32 g (13%), highly viscous yellow oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 2930 cm^{-1}, 2860, 1703, 1665, 1450. – ^{1}H NMR ($CDCl_3$): δ = 0.8–2.7 (m, 19H), 2.65 (d, ^2J = 11 Hz, 1H, 11-H_a), 2.75–2.83 (m, 2H, CH), 6.0–6.1 (m, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 20.7 (t), 26.5 (t), 27.1 (t), 27.3 (t), 27.5 (t), 28.4 (t), 29.1 (t), 33.9 (t), 37.2 (t), 42.8 (d), 46.5 (d), 47.0 (d), 48.9 (d), 56.5 (s), 137.2 (d, C-3), 137.3 (d, C-4), 218.0 (s, C-10). – MS (70 eV): *m/z* (%) = 244 (26), [M^+], 177 (100), 161 (12), 150 (14), 149 (16), 135 (33), 98 (55).

Attempted Cycloaddition of **14** *to Furan:* Dibromo ketone **14** (6.76 g, 20 mmol) and furan (5.44 g, 80 mmol) were allowed to react according to the general procedure, giving *6-cyclohexyl-2-(2-furyl)-cyclohexanone* (**14a**); 0.35 g (7%). – IR ($CHCl_3$): $\tilde{\nu}$ = 2930 cm^{-1}, 2860, 1710, 1445, 1190, 1115, 940. – ^{1}H NMR ($CDCl_3$): δ = 0.8–2.4 (m, 18H), 3.70 (dd, *J* = 12 Hz, *J* = 5 Hz, 1H, H_d), 6.25 (dt, *J* = 3 Hz, *J* = 2 Hz, 1H, H_c), 6.35 (dd, *J* = 3 Hz, *J* = 2 Hz, 1H, H_b), 7.35 (dd, *J* = 2 Hz, *J* = 1 Hz, 1H, H_a). – MS (70 eV, 80°C): *m/z* (%) = 246 (100) [M^+], 178 (23), 164 (89), 135 (37), 108 (25).

(7R)-1-Isopropyl-7-methyl-11-oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-one [(7*R*)-**6**]: (5*R*)-2,6-Dibromo-2-isopropyl-5-methylcyclohexanone (1.56 g, 5.0 mmol) and furan (1.36 g, 20 mmol) were allowed to react following the general procedure, giving (7*R*)-**6**; 0.25 g (22%),

fine needles, m.p. 83°C, $[\alpha]_D^{23} = +10.99$ ($c = 1.31$ in CH_2Cl_2). – IR ($CHCl_3$): $\tilde{\nu} = 2970\ cm^{-1}$, 2940, 2880, 1710. – ^1H NMR ($CDCl_3$): $\delta = 0.85$ (d, $J = 7$ Hz, 3H, CH_3), 1.00 (t, $J = 7$ Hz, 3H, isopropyl-CH_3), 1.0–2.7 (m, 7H), 4.70 (s, 1H, 2-H), 4.80 (dd, $J = 1$ Hz, $J = 2$ Hz, 1H, 5-H), 6.30 (t, $J = 1$ Hz, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): $\delta = 17.3$ (q, isopropyl-CH_3), 18.4 (q, isopropyl-CH_3), 22.9 (q, CH_3), 28.2 (d, C-7), 28.7 (t, C-8), 30.9 (t, C-9), 36.1 (d, isopropyl-CH), 59.7 (s, C-1), 59.8 (d, C-6), 83.1 (d, C-5), 84.8 (d, C-2), 133.9 (d, C-3), 134.8 (d, C-4), 212.5 (s, C-10). – MS (70 eV): *m/z* (%) = 220 (94) [M^+], 205 (85), 177 (52), 176 (81), 163 (37), 152 (31), 149 (44), 137 (46), 108 (100).

$C_{14}H_{20}O_2$ (220.1) Calcd. C 76.33 H 9.15 Found C 76.00 H 9.10
Calcd. 220.1463 Found 220.1463 (MS)

1-Isopropyl-7-methyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-one (**7**): 2,6-Dibromo-2-isopropyl-5-methylcyclohexanone (1.56 g, 5.0 mmol) and cyclopentadiene (0.86 g, 13 mmol) were allowed to react according to the general procedure, giving **7**; 0.33 g (30%), yellow oil. – IR ($CHCl_3$): $\tilde{\nu} = 3000\ cm^{-1}$, 2960, 2880, 1700, 1665, 1450. – ^1H NMR ($CDCl_3$): $\delta = 0.85$ (d, $J = 7$ Hz, 3H, CH_3), 0.95 (d, $J = 6$ Hz, 3H, isopropyl-CH_3), 1.00 (d, $J = 6$ Hz, 3H, isopropyl-CH_3), 1.65–2.30 (m, 8H), 2.55 (d, $^2J = 12$ Hz, 1H, 11-H_a), 2.70–2.80 (m, 2H, methine-H), 6.10 (d, $J = 1$ Hz, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): $\delta = 18.1$ (q, isopropyl-CH_3), 18.3 (q, isopropyl-CH_3), 24.6 (q, CH_3), 30.7 (t), 30.8 (d + t), 36.1 (d), 37.4 (t), 46.0 (d), 47.5 (d), 55.7 (s, C-1), 57.6 (d), 136.6 (d, C-3), 137.3 (d, C-4), 216.6 (s, C-10). – MS (70 eV): *m/z* (%) = 218 (51) [M^+], 203 (74), 185 (15), 174 (22), 152 (100), 137 (75).

$C_{15}H_{22}O$ Calcd. 218.1671 Found 218.1721 (MS)

(7S)-7-Isopropyl-1-methyl-11-oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-one [(7*S*)-**8**]: Furan (2.72 g, 40 mmol) and (5*S*)-2,6-dibromo-5-isopropyl-2-methylcyclohexanone (3.74 g, 12 mmol) were allowed to react according to the general procedure, giving (7*S*)-**8**; 0.71 g (27%), yellow oil, $[\alpha]_D^{20} = +26.4$ ($c = 2.89$ g in CH_2Cl_2). – IR ($CHCl_3$): $\tilde{\nu} = 2965\ cm^{-1}$, 2875, 1720, 1460, 1375, 1315, 1200, 1115. – ^1H NMR ($CDCl_3$): $\delta = 0.86$ (d, $J = 7$ Hz, 3H, isopropyl-CH_3), 0.87 (d, $J = 7$ Hz, 3H, isopropyl-CH_3), 0.90 (s, 3H, CH_3), 1.00–2.55 (m, 7H), 4.40 (s, 1H, 2-H), 4.70 (d, $J = 2$ Hz, 1H, 5-H), 6.30 (s, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): $\delta = 18.6$ (q, isopropyl-CH_3), 19.3 (q, isopropyl-CH_3), 19.8 (q, CH_3), 24.7 (t, C-8), 32.9 (d, isopropyl-CH), 36.1 (t, C-9), 47.0 (d, C-7), 52.4 (s, C-1), 54.9 (d, C-6), 83.5 (d, C-5), 86.6 (d, C-2), 133.9 (d, C-3), 135.2 (d, C-4), 213.0 (s, C-10). – MS (70 eV): *m/z* (%) = 220 (44) [M^+], 179 (13), 176 (36), 150 (100), 121 (38), 110 (81), 107 (35), 82 (53).

$C_{14}H_2O_2$ Calcd. 220.1463 Found 220.1463 (MS)

(7S)-7-Isopropyl-1-methyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-one [(7*S*)-**9**]: Cyclopentadiene (0.74 g, 11.2 mmol) and (5*S*)-2,6-dibromo-5-isopropyl-2-methylcyclohexanone (1.40 g, 4.50 mmol) were allowed to react according to the general procedure, giving (7*S*)-**9**; 0.41 g (41%), yellow oil. – IR ($CHCl_3$): $\tilde{\nu} = 3000\ cm^{-1}$, 2960, 2940, 2875, 1708, 1665, 1455. – ^1H NMR ($CDCl_3$): $\delta = 0.84$ (d, $J = 7$ Hz, 3H, isopropyl-CH_3), 0.86 (d, $J = 7$ Hz, 3H, isopropyl-CH_3), 0.95 (s, 3H, CH_3), 1.00–1.95 (m, 6H), 2.10–2.35 (m, 2H), 2.40–2.45 (m, 1H), 2.60 (d, $J = 12$ Hz, 1H, 11-H_a), 2.65–2.75 (m, 1H, bridgehead-H), 6.05–6.15 (m, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): $\delta = 19.2$ (q, isopropyl-CH_3), 19.7 (q, isopropyl-CH_3), 23.1 (q, CH_3), 24.2 (t, C-8), 34.2 (d, isopropyl-CH), 36.7 (t, C-9), 37.1 (t, C-11), 46.5 (d, C-7), 47.5 (d, bridgehead), 49.1 (s, C-1), 52.2 (d, bridgehead), 52.8 (d, bridgehead), 136.6 (d, C-3), 137.8 (d, C-4), 217.6 (s, C-10). – MS (70 eV): *m/z* (%) = 218 (82) [M^+], 174 (36), 153 (80), 97 (100).

$C_{15}H_{22}O$ Calcd. 218.1671 Found 218.1670 (MS)

1,6-Dimethyl-11-oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-one (**10**): 2,6-Dibromo-2,6-dimethylcyclohexanone (1.42 g, 5.0 mmol) and furan (1.36 g, 20 mmol) were allowed to react according to the general procedure, giving **10**; 0.21 g (22%), very fine platelets, m.p. 57°C. – IR (KBr): $\tilde{\nu} = 2926\ cm^{-1}$, 1718, 1375, 1049, 941, 716. – ^1H NMR ($CDCl_3$): $\delta = 0.90$ (s, 6H, CH_3), 1.0–2.75 (m, 6H), 4.60 (s, 2H, 2-H), 6.40–6.45 (m, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): $\delta = 18.3$ (q, CH_3), 21.5 (t, C-8), 40.2 (t, C-7, C-9), 87.7 (d, C-2, C-5), 135.8 (d, C-3, C-4), 215.2 (s, C-10). – MS (70 eV): *m/z* (%) = 192 (48) [M^+], 176 (100), 149 (9), 124 (22), 109 (14), 108 (12), 96 (9), 95 (12), 82 (22), 70 (33).

$C_{12}H_{16}O_2$ (192.1) Calcd. C 74.97 H 8.39 Found C 74.98 H 9.38
Calcd. 192.1150 Found 192.1149 (MS)

1,6-Dimethyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-one (**11**): Dibromoketone **17** (2.84 g, 10 mmol) and cyclopentadiene (1.58 g, 24 mmol) were allowed to react following the general procedure, giving **11**; 0.35 g (18%), yellow wax, m.p. 62°C. – IR ($CHCl_3$): $\tilde{\nu} = 2970\ cm^{-1}$, 2940, 2870, 1720, 1455, 1375. – ^1H NMR ($CDCl_3$): $\delta = 0.95$ (s, 6H, CH_3), 1.3–2.3 (m, 7H), 2.40–2.55 (m, 2H, 2-H, 5-H), 2.75 (d, $^2J = 11$ Hz, 1H, 11-H_a), 6.10–6.20 (m, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): $\delta = 19.7$ (t, C-8), 23.4 (q, CH_3), 38.0 (t, C-11), 38.1 (t, C-7, C-9), 49.1 (s, C-1, C-6), 52.4 (d, C-2, C-5), 137.7 (d, C-3, C-4), 218.5 (s, C-10). – MS (70 eV): *m/z* (%) = 190 (43) [M^+], 174 (13), 147 (9), 125 (100).

$C_{13}H_{18}O$ Calcd. 190.1358 Found 190.1358 (MS)

General Procedure for the Reduction of the Tricyclic Ketones with LiAlH$_4$: The Cycloadduct (4 mmol) in ether (16 ml) was added slowly dropwise to a suspension of $LiAlH_4$ (76 mg, 2 mmol) in anhydrous ether (6.0 ml). After being stirred for 2 h at room temp. (longer reaction times lead to overreduction, i.e. disappearance of the olefinic double bond), the mixture was treated with water (0.1 ml), 15% aqueous NaOH (0.1 ml), and finally water (0.3 ml). The precipitate was filtered off, washed with ether (40 ml), and the filtrate was dried ($MgSO_4$). After removal of the solvent, the resulting crude yellow oil was chromatographed [silica gel, light petroleum ether/ether (12:1)].

1-Cyclohexyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol (**19**): 605 mg (62%); rods and platelets, m.p. 78°C. – IR ($CHCl_3$): $\tilde{\nu} = 3580\ cm^{-1}$, 2930, 2860, 1448, 1190, 1060, 1040. – ^1H NMR ($CDCl_3$): $\delta = 0.80–2.10$ (m, 20H), 2.45 (d, $^2J = 11$ Hz, 1H, 11-H_a), 2.50–2.70 (m, 2H, methine-H), 3.70 (s, 1H, 10-H), 6.40–6.50 (m, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): $\delta = 18.1$ (t), 25.9 (t), 27.0 (t), 27.1 (t), 27.15 (t), 27.4 (t), 28.0 (t), 29.2 (t), 37.5 (d, cyclohexyl-CH), 38.9 (t, C-11), 42.7 (s, C-1), 43.3 (d), 45.0 (d), 46.1 (d), 74.9 (d, C-10), 140.1 (d, C-3), 141.3 (d, C-4). – MS (70 eV): *m/z* (%) = 246 (20) [M^+], 228 (20), 219 (10), 201 (10), 180 (41), 145 (25), 111 (40), 98 (100).

$C_{17}H_{26}O$ (246.2) Calcd. C 82.87 H 10.64 Found C 82.20 H 10.45
Calcd. 246.1984 Found 246.1984 (MS)

(7R)- and (7S)-1-Isopropyl-7-methyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol [(7*R*)-**20** and (7*S*)-**20**]: Tricyclic ketone (7*R*)-**7** (0.98 g, 4.5 mmol) and (7*S*)-**7** (0.98 g, 4.5 mmol) were treated separately with $LiAlH_4$ (0.09 g, 2.3 mmol) according to the general procedure, giving (7*R*)-**20** and (7*S*)-**20**, each 0.74 g (75%); light yellow feathery crystals, m.p. 64°C, $[\alpha]_D^{20} = -48.8$ ($c = 1.87$ in CH_2Cl_2) for (7*R*)-**20** and $[\alpha]_D^{25} = +42.6$ ($c = 2.99$ in CH_2Cl_2) for (7*S*)-**20**. – IR ($CHCl_3$): $\tilde{\nu} = 3600\ cm^{-1}$, 3000, 2930, 2880, 1665, 1455, 1380. – ^1H NMR ($CDCl_3$): $\delta = 0.85$ (d, $J = 7$ Hz, 3H, isopropyl-CH_3), 0.90 (d, $J = 7$ Hz, 3H, isopropyl-CH_3), 1.00 (d, $J = 6$ Hz, 3H, CH_3), 0.9–2.0 (m, 8H), 2.30 (d, $J = 11$ Hz, 1H, 11-H_a), 2.45–2.55 (m, 2H, 2-H, 5-H), 2.75 (d, $J = 11$ Hz, 1H, OH), 3.72 (d, $J = 11$ Hz, 1H, 10-H), 6.35–6.45 (m, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): $\delta = 16.1$ (q, isopropyl-CH_3), 17.4 (q, isopropyl-CH_3), 24.9 (q, CH_3), 27.5 (t), 27.8 (t), 31.9 (d), 33.8 (d), 39.1 (t, C-11), 41.7 (s, C-1), 44.3 (d), 44.7

(d), 46.2 (d), 71.3 (d, C-10), 139.7 (d, C-3), 140.9 (d, C-4). – MS (70 eV): *m/z* (%) = 220 (15) [M$^+$], 202 (20), 186 (7), 158 (29), 154 (65), 139 (100).

$C_{15}H_{24}O$ Calcd. 220.1827 Found 220.1826 (MS)

(7S)-7-Isopropyl-1-methyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol [(7*S*)-**21**]: Ketone (7*S*)-**9** (436 mg, 2 mmol) was reduced with $LiAlH_4$ (76.0 mg, 2 mmol) following the general procedure, giving (7*S*)-**21**; 364 mg (83%), oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 3580 cm^{-1}, 3000, 2960, 2940, 2870, 1450, 1065. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (d, *J* = 6 Hz, 3H, isopropyl-CH_3), 0.90 (d, *J* = 6 Hz, 3H, isopropyl-CH_3), 1.00 (s, 3H, CH_3), 1.10–1.80 (m, 8H), 1.80–1.90 (m, 1H), 2.05 (br. s, 1H, 2-H), 2.35–2.45 (m, 1H, 5-H), 2.35 (d, *J* = 12 Hz, 1H, 11-H_a), 2.70 (d, *J* = 12 Hz, 1H, OH), 3.50 (d, *J* = 12 Hz, 1H, 10-H), 6.35 (dd, *J* = 5 Hz, *J* = 3 Hz, 1H, 4-H), 6.40 (dd, *J* = 5 Hz, *J* = 3 Hz, 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 19.2 (q, isopropyl-CH_3), 19.6 (q, isopropyl-CH_3), 21.8 (t, C-8), 27.5 (q, CH_3), 34.1 (d, isopropyl-CH), 36.4 (s, C-1), 36.6 (t, C-9), 39.5 (t, C-11), 39.7 (d, C-7), 45.0 (d), 45.7 (d), 50.3 (d), 75.1 (d, C-10), 139.9 (d, C-3), 140.5 (d, C-4). – MS (70 eV): *m/z* (%) = 220 (15) [M$^+$], 202 (23), 186 (6), 176 (5), 159 (12), 154 (8), 137 (11), 112 (100), 81 (14).

$C_{15}H_{24}O$ Calcd. 220.1827 Found 220.1826 (MS)

1,6-Dimethyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol (**22**): Ketone **11** (95 mg, 0.50 mmol) and $LiAlH_4$ (10 mg, 0.26 mmol) were allowed to react according to the general procedure, giving **22**; 70 mg (73%), viscous oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 3590 cm^{-1}, 2980, 2930, 2870, 1450, 1380. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (s, 6H, CH_3), 0.9–2.0 (m, 7H), 2.10 (s, 1H, OH), 2.20–2.30 (m, 2H, 2-H, 5-H), 2.60 (d, *J* = 11 Hz, 1H, 11-H_a), 3.20 (s, 1H, 10-H), 6.45 (br. s, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 19.1 (t, C-8), 27.1 (q, CH_3), 37.9 (s, C-1, C-6), 38.0 (t, C-7, C-9), 39.6 (t, C-11), 50.4 (d, C-2, C-5), 82.9 (d, C-10), 141.0 (d, C-3, C-4). – MS (70 eV): *m/z* (%) = 192 (47) [M$^+$], 174 (12), 158 (8), 147 (15), 126 (100), 109 (91).

$C_{13}H_{20}O$ Calcd. 192.1514 Found 192.1513 (MS)

1-Methyl-11-oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol (**23**): Ketone **3** (327 mg, 1.84 mmol) and $LiAlH_4$ (35.0 mg, 0.92 mmol) were allowed to react according to the general procedure, giving **23**; 234 mg (71%), wax, m.p. 37°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 3600 cm^{-1}, 3000, 2930, 2870, 1450, 1420, 1375. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 3H, CH_3), 1.1–2.0 (m, 6H), 2.30–2.60 (m, 2H, 6-H, OH), 3.40 (br. d, *J* = 6 Hz, 1H, 10-H), 4.35 (t, *J* = 2 Hz, 1H, 4-H), 4.75 (dd, *J* = 3 Hz, *J* = 2 Hz, 1H, 5-H), 6.65 (dd, *J* = 6 Hz, *J* = 2 Hz, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 21.7 (q, CH_3), 21.8 (t, C-8), 30.2 (t, C-7), 39.8 (t, C-9), 39.9 (d, C-6), 40.1 (s, C-1), 79.3 (d, C-5), 82.7 (d, C-2), 86.7 (d, C-10), 137.5 (d, C-3), 138.1 (d, C-4). – MS (70 eV): *m/z* (%) = 180 (3) [M$^+$], 162 (26), 152 (24), 147 (33), 134 (13), 112 (59), 97 (100), 95 (99), 94 (42), 84 (40), 79 (40), 70 (54).

$C_{11}H_{16}O_2$ Calcd. 180.1150 Found 180.1151 (MS)

(7R)-1-Isopropyl-7-methyl-11-oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol (**24**): Ketone (7*R*)-**6** (550 mg, 2.50 mmol) was reduced with $LiAlH_4$ (47.0 mg, 1.25 mmol), giving **24**; 420 mg (76%), fine needles, m.p. 80°C, $[\alpha]_D^{20}$ = –39.4 (*c* = 0.94 in CH_2Cl_2). – IR ($CHCl_3$): $\tilde{\nu}$ = 3600 cm^{-1}, 3010, 2960, 2880, 1455. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (d, *J* = 7 Hz, 3H, isopropyl-CH_3), 0.90 (d, *J* = 7 Hz, 3H, isopropyl-CH_3), 1.05 (d, *J* = 7 Hz, 3H, CH_3), 0.90–1.80 (m, 6H), 2.10–2.35 (m, 2H, 2-H, 5-H), 2.50 (br. s, 1H, OH), 3.80 (br. s, 1H, 10-H), 4.55 (t, *J* = 2 Hz, 1H, 2-H), 4.60 (dt, *J* = 2 Hz, *J* = 2 Hz, 1H, 5-H), 6.60 (2 dd, *J* = 7 Hz, *J* = 2 Hz, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 15.9 (q, isopropyl-CH_3), 16.7 (q, isopropyl-CH_3), 23.0 (q, CH_3), 26.3 (t), 28.7 (t), 29.0 (d), 33.6 (d), 43.6 (s, C-1), 46.0 (d, C-6), 70.3 (d, C-10), 82.5 (d, C-5), 84.0 (d, C-2), 136.7 (d, C-3), 137.8 (d, C-4). – MS (70 eV): *m/z* (%) = 222 (8) [M$^+$], 204 (21), 161 (10), 160 (23), 154 (45), 139 (100), 137 (35).

$C_{14}H_{22}O_2$ (222.2) Calcd. C 75.63 H 9.97 Found C 75.64 H 9.93
Calcd. 222.1620 Found 222.1620 (MS)

(7S)-7-Isopropyl-1-methyl-11-oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol [(7*S*)-**25**]: Ketone (7*S*)-**8** (440 mg, 2 mmol) was treated with $LiAlH_4$ (38.0 mg, 1 mmol) following the general procedure, giving (7*S*)-**25**; 364 mg (83%), fine needles, m.p. 37°C, $[\alpha]_D^{19}$ = –32.4 (*c* = 1.00 in CH_2Cl_2). – IR ($CHCl_3$): $\tilde{\nu}$ = 3600 cm^{-1}, 3000, 2960, 2870, 1455, 1060, 1030. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 3H, CH_3), 0.90 (2 d, *J* = 7 Hz, 6H, isopropyl-CH_3), 0.90–2.10 (m, 7H), 2.60 (br. s, 1H, OH), 3.45 (dd, *J* = 3 Hz, *J* = 2 Hz, 1H, 10-H), 4.10 (t, *J* = 2 Hz, 1H, 2-H), 4.45 (dd, *J* = 4 Hz, *J* = 2 Hz, 1H, 5-H), 6.55 (2 dd, *J* = 6 Hz, *J* = 2 Hz, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 19.9 (q, isopropyl-CH_3), 20.8 (q, isopropyl-CH_3), 22.4 (q, CH_3), 23.5 (t, C-8), 32.2 (d), 36.5 (t, C-9), 38.3 (s, C-1), 41.2 (d), 45.5 (d, C-6), 73.4 (d, C-10), 82.9 (d, C-5), 86.1 (d, C-2), 136.9 (d, C-3), 137.7 (d, C-4). – MS (70 eV): *m/z* (%) = 222 (5) [M$^+$], 204 (10), 136 (21), 134 (20), 111 (100).

$C_{14}H_{22}O_2$ (222.2) Calcd. C 75.63 H 9.97 Found C 75.32 H 10.61
Calcd. 222.1620 Found 222.1620 (MS)

1,10-Dimethyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol (**26**): A 1.6 N solution (6.25 ml, 10 mmol) of methyllithium in ether was added slowly dropwise over 45 min to a suspension of *t*BuOK (1.34 g, 11 mol) in absolute ether (6 ml), maintained under N_2 at –78°C in a previously flame-dried apparatus. The mixture was stirred for a further hour at –78°C, and then ketone **4** (176 mg, 1 mmol) in anhydrous ether (4 ml) was added dropwise over 30 min. The resulting suspension was stirred and allowed to reach room temp. (ca. 12 h) and then recooled to 0°C. After hydrolysis with 20% aqueous NH_4Cl (8 ml), the organic phase was separated, and the aqueous phase was brought to pH = 8 by addition of satd. aqueous NH_4Cl. The aqueous layer was extracted with ether (4 × 10 ml), and the combined organic phases were washed with satd. aqueous NaCl (2 × 15 ml) and dried (Na_2SO_4). After removal of the solvent, the crude brown product was purified by chromatography [silica gel, light petroleum ether/ether (12:1)] giving **26**; 55 mg (32%), colorless oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 3570 cm^{-1}, 3000, 2940, 1490, 1460, 1385, 1370, 1350, 1120. – ^{1}H NMR ($CDCl_3$): δ = 0.90 (s, 3H, 12-H), 1.15 (d, ^4J = 2 Hz, 3H, 13-H), 0.9–2.3 (m, 10H), 2.55 (d, *J* = 11 Hz, 1H, 11-H_a), 2.55–2.65 (m, 1H), 3.80 (q, ^4J = 2 Hz, 1H, OH), 6.55 (2 dd, *J* = 7 Hz, *J* = 3 Hz, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 18.5 (t, C-8), 23.4 (q, C-14), 25.3 (q, C-13), 26.9 (t, C-7), 36.6 (t, C-9), 40.2 (t, C-11), 40.8 (s, C-1), 42.1 (d), 46.6 (d), 52.9 (d, C-2), 77.6 (s, C-10), 141.4 (d, C-3), 142.2 (d, C-4). – MS (70 eV): *m/z* (%) = 192 (45) [M$^+$], 176 (9), 174 (34), 159 (37), 111 (51), 110 (100), 108 (77).

$C_{13}H_{20}O$ Calcd. 192.1514 Found 192.1513 (MS)

1,6,10-Trimethyltricyclo[4.3.1.1^{2,5}]undec-3-en-10-ol (**27**): Ketone **11** (95.0 mg, 0.5 mmol) was allowed to react with *t*BuOK (620 mg, 55 mmol) and a 1.6 N solution of methyllithium in ether (3.12 ml, 5.0 mmol) as described above, giving **27**; 29.0 mg (28%), viscous oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 3570 cm^{-1}, 2940, 1455, 1115. – ^{1}H NMR ($CDCl_3$): δ = 0.90 (s, 6H, 12-H, 13-H), 1.10 (d, ^4J = 2 Hz, 3H, 14-H), 1.5–2.0 (m, 6H), 2.15–2.25 (m, 3H, 2-H, 5-H, 11-H_b), 2.55 (d, *J* = 11 Hz, 1H, 11-H_a), 3.30 (q, ^4J = 2 Hz, 1H, OH), 6.55 (s, 2H, 3-H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 19.1 (t, C-8), 21.0 (q, C-14), 23.6 (q, C-12, C-13), 36.3 (t, C-7, C-9), 40.5 (s, C-1, C-6), 40.3 (t, C-11), 53.4 (d, C-2, C-5), 79.7 (s, C-10), 141.8 (d, C-3, C-4). – MS (70 eV): *m/z* (%) = 206 (32) [M$^+$], 190 (6), 188 (6), 172 (10), 140 (14), 123 (100).

$C_{14}H_{22}O$ Calcd. 206.1671 Found 206.1671 (MS)

General Procedure for the Hydrogenation of the Tricyclic Alcohols: The tricyclic alcohol (1.0 mmol) in methanol (5 ml) was hydrogenated at atmospheric pressure using Pt on charcoal (0.05 g, 5% Pt). After 1.0–1.5 h the reaction was complete, the catalyst was filtered off, the methanol was evaporated, and the light yellow crude product was chromatographed [silica gel, light petroleum ether/ethyl acetate (12:1)].

1-Cyclohexyltricyclo[4.3.1.1^{2,5}]undecan-10-ol (**28**): The alcohol **19** (369 mg, 1.5 mmol) was hydrogenated, giving **28**; 190 mg (51%), very fine platelets, m.p. 69°C. – IR (KBr): $\tilde{\nu}$ = 3479 cm^{-1}, 2926, 2855, 1450, 1044. – ^{1}H NMR ($CDCl_3$): δ = 0.75–2.20 (m, 27H), 3.70 (s, 1H, 10-H). – ^{13}C NMR ($CDCl_3$): δ = 18.0 (t), 25.1 (t), 25.6 (t), 26.7 (t), 27.1 (t), 27.2 (t), 27.4 (t), 28.2 (t), 29.7 (t), 29.9 (t), 32.5 (t), 40.4 (d), 40.6 (d), 40.9 (d), 41.4 (d), 41.5 (s, C-1), 73.8 (d, C-10). – MS (70 eV): *m/z* (%) = 248 (14) [M$^+$], 233 (11), 230 (100), 202 (7), 179 (10), 165 (28), 163 (33), 147 (46), 98 (91).

$C_{17}H_{28}O$ (248.2) Calcd. C 82.94 H 10.64 Found C 82.57 H 10.51
Calcd. 248.2140 Found 248.2140 (MS)

(7R)- and (7S)-1-Isopropyl-7-methyltricyclo[4.3.1.1^{2,5}]undecan-10-ol [(7*R*)-**29** and (7*S*)-**29**]: Alcohols (7*R*)-**20** and (7*S*)-**20** (220 mg, 1.0 mmol) were hydrogenated separately, giving (7*R*)-**29** and (7*S*)-**29**; 165 mg (74%) each, soft waxy platelets, m.p. 32°C, $[\alpha]_D^{20}$ = +10.69 (*c* = 0.87 in CH_2Cl_2) for (7*R*)-**29** and $[\alpha]_D^{20}$ = –10.85 (*c* = 2.17 in CH_2Cl_2) for (7*S*)-**29**. – IR ($CHCl_3$): $\tilde{\nu}$ = 3630 cm^{-1}, 2950, 2880, 1470. – ^{1}H NMR ($CDCl_3$): δ = 0.76 (d, *J* = 7 Hz, 3H, CH_3), 0.90 (d, *J* = 7 Hz, 3H, isopropyl-CH_3), 0.95 (d, *J* = 7 Hz, 3H, isopropyl-CH_3), 1.0–2.2 (m, 16H), 3.72 (br. s, 1H, 10-H). – ^{13}C NMR ($CDCl_3$): δ = 16.0 (q, isopropyl-CH_3), 16.9 (q, isopropyl-CH_3), 24.6 (t), 24.8 (q, CH_3), 27.1 (t), 27.6 (t), 27.9 (t), 28.9 (d), 32.2 (t, C-11), 35.1 (d), 40.4 (d), 40.5 (s, C-1), 41.7 (d), 47.9 (d), 70.1 (d, C-10). – MS (70 eV): *m/z* (%) = 222 (5) [M$^+$], 204 (36), 188 (31), 161 (100).

$C_{15}H_{26}O$ (222.2) Calcd. C 81.02 H 11.78 Found C 81.14 H 11.76
Calcd. 222.1984 Found 222.1984 (MS)

(7S)-7-Isopropyl-1-methyltricyclo[4.3.1.1^{2,5}]undecan-10-ol [(7*S*)-**30**]: The alcohol (7*S*)-**21** (286 mg, 1.3 mmol) was hydrogenated, giving (7*S*)-**30**; 180 mg (62%), semicrystalline oil, $[\alpha]_D^{24}$ = +14.94 (*c* = 0.87 in CH_2Cl_2). – IR ($CHCl_3$): $\tilde{\nu}$ = 3620 cm^{-1}, 2960, 2930, 2880, 1460. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (d, *J* = 7 Hz, 3H, isopropyl-CH_3), 0.90 (d, *J* = 7 Hz, 3H, isopropyl-CH_3), 0.95 (s, 3H, CH_3), 1.00–1.80 (m, 12H), 1.85–2.10 (m, 4H), 3.50 (br. s, 1H, 10-H). – ^{13}C NMR ($CDCl_3$): δ = 19.3 (q, isopropyl-CH_3), 19.7 (q, isopropyl-CH_3), 20.9 (t, C-8), 25.4 (t), 26.1 (q, CH_3), 27.6 (t), 32.3 (t), 34.1 (d, isopropyl-CH), 35.8 (s, C-1), 36.8 (t, C-11), 41.2 (d), 42.6 (d), 46.2 (d), 47.0 (d), 74.4 (d, C-10). – MS (70 eV): *m/z* (%) = 222 (11) [M$^+$], 220 (19), 204 (58), 188 (15), 178 (10), 161 (100), 138 (71), 137 (80), 111 (98).

$C_{15}H_{26}O$ Calcd. 222.1984 Found 222.1975 (MS)

(7R)-1-Isopropyl-7-methyl-11-oxatricyclo[4.3.1.1^{2,5}]undecan-10-ol [(7*R*)-**31**]: The alcohol (7*R*)-**24** (320 mg, 1.5 mmol) was hydrogenated, giving (7*R*)-**31**; 300 mg (92%), heavy rods, m.p. 180°C, $[\alpha]_D^{23}$ = +12.90 (*c* = 0.47 in CH_3OH). – IR (KBr): $\tilde{\nu}$ = 3351 cm^{-1}, 2948, 2884, 1462. – ^{1}H NMR (CD_3OD): δ = 0.80 (d, *J* = 7 Hz, 3H, 14-H), 0.90 (d, *J* = 7 Hz, 3H, 13-H), 1.00 (d, *J* = 7 Hz, 3H, 15-H), 1.00–1.85 (m, 7H), 1.90–2.20 (m, 3H), 2.25–2.45 (m, 2H), 3.80 (m, 1H, 10-H), 4.10 (2 t, *J* = 7 Hz, 2H, 2-H, 5-H). – ^{13}C NMR (CD_3OD): δ = 15.9 (q, C-14), 16.7 (q, C-13), 23.5 (q, C-15), 25.6 (t, C-8), 27.6 (t, C-9), 28.7 (t, C-3), 29.0 (d), 29.1 (t, C-4), 36.3 (d), 42.7 (s, C-1), 49.1 (d, C-6), 68.7 (d, C-10), 80.8 (d, C-5), 82.5 (d, C-2). – MS (70 eV): *m/z* (%) = 224 (1) [M$^+$], 212 (18), 206 (5), 202 (5), 138 (100), 95 (30), 87 (69).

$C_{14}H_{24}O_2$ (224.2) Calcd. C 74.95 H 10.78 Found C 75.00 H 10.62
Calcd. 224.1776 Found 224.1776 (MS)

(7S)-7-Isopropyl-1-methyl-11-oxatricyclo[4.3.1.1^{2,5}]undecan-10-ol [(7*S*)-**32**]: The alcohol (7*S*)-**25** (444 mg, 2.0 mmol) was hydrogenated, giving (7*S*)-**32**; 385 mg (86%), needles, m.p. 98°C, $[\alpha]_D^{19}$ = –11.0 (*c* = 1.50 in CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 3401 cm^{-1}, 3011, 2943, 2930, 2870, 1460, 1385, 1369, 1327. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 3H, CH_3), 0.90 (2 d, *J* = 7 Hz, 6H, isopropyl-CH_3), 1.1–2.0 (m, 9H), 2.15–2.30 (m, 2H), 2.35 (s, 1H, OH), 3.60 (s, 1H, 10-H), 3.70 (d, *J* = 7 Hz, 1H, 2-H), 4.00 (d, *J* = 7 Hz, 1H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 20.0 (q, C-15), 20.9 (q, C-14), 22.5 (q, C-12), 22.7 (t, C-8), 25.5 (t, C-9), 28.0 (t, C-3), 32.3 (d, C-13), 36.9 (t, C-4), 37.0 (s, C-1), 42.9 (d, C-7), 47.1 (d, C-6), 72.4 (d, C-10), 79.7 (d, C-5), 83.1 (d, C-2). – MS (70 eV): *m/z* (%) = 224 (3) [M$^+$], 222 (3), 206 (5), 163 (2), 145 (4), 139 (13), 138 (100), 123 (16), 95 (42), 87 (91), 72 (45).

$C_{14}H_{24}O_2$ (224.2) Calcd. C 74.95 H 10.78 Found C 75.15 H 10.71
Calcd. 224.1776 Found 224.1776 (MS)

1,10-Dimethyltricyclo[4.3.1.1^{2,5}]undecan-10-ol (**33**): The alcohol **26** (96 mg, 0.5 mmol) was hydrogenated, giving **33**; 66 mg (68%), oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 3400 cm^{-1}, 2940, 2880, 1460, 1100. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 3H, 12-H), 1.20 (s, 3H, 13-H), 0.9–2.5 (m, 16H). – ^{13}C NMR ($CDCl_3$): δ = 18.2 (t, C-8), 21.9 (q, C-12), 26.7 (t), 27.5 (q, C-13), 28.3 (t), 28.8 (t), 33.0 (t), 37.8 (t, C-11), 39.4 (s, C-1), 43.0 (d), 45.0 (d), 48.8 (d), 76.9 (s, C-10). – MS (70 eV): *m/z* (%) = 194 (100) [M$^+$], 195 (17), 178 (16), 176 (7), 161 (18), 150 (10), 147 (11), 146 (9), 136 (23), 133 (20), 123 (65).

$C_{13}H_{22}O$ Calcd. 194.1671 Found 194.1670 (MS)

1,6,10-Trimethyltricyclo[4.3.1.1^{2,5}]undecan-10-ol (**34**): The alcohol **27** (80 mg, 0.4 mmol) was hydrogenated, giving **34**; 51 mg (63%), oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 2940 cm^{-1}, 1460, 1375, 1100. – ^{1}H NMR ($CDCl_3$): δ = 0.90 (s, 6H, 12-H, 13-H), 1.15 (s, 3H, 14-H), 1.0–2.5 (m, 15H). – ^{13}C NMR ($CDCl_3$): δ = 18.9 (t, C-8), 22.0 (q, C-12, C-13), 22.9 (q, C-14), 27.0 (t, C-7, C-9), 33.8 (t, C-3, C-4), 37.6 (t, C-11), 40.2 (s, C-1, C-6), 49.3 (d, C-2, C-5), 78.6 (s, C-10). – MS (70 eV): *m/z* (%) = 208 (13) [M$^+$], 193 (100), 189 (18), 174 (46), 164 (55), 123 (49), 109 (52), 95 (73).

$C_{14}H_{24}O$ Calcd. 208.1827 Found 208.1828 (MS)

X-ray Structure Analysis of **31**: $C_{14}H_{24}O_2$, mol. mass 224.3 g/mol, orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 896.7(1), *b* = 1189.9(2), *c* = 1205.7(2) pm, *V* = 1286.5(4) · 10^6 pm^3, *Z* = 4, D_x = 1.16 g/cm^3, μ = 0.7 cm^{-1}, Stoe-Siemens AED2 four-circle diffractometer, Mo-K_α radiation, λ = 71.073 pm, graphite mono-

Table 1. Atomic coordinates and parameters of the isotropic equivalent of the temperature factor [pm^2] of the nonhydrogen atoms of **31**

Atom	*x*	*y*	*z*	U_{eq}
C1	0.54357(37)	0.47309(29)	0.37276(29)	455(11)
C2	0.58447(39)	0.54431(31)	0.47538(32)	521(13)
C3	0.63045(46)	0.66537(35)	0.44909(43)	673(16)
C4	0.80003(57)	0.65725(42)	0.43365(52)	851(20)
C5	0.83111(46)	0.53315(41)	0.44926(35)	680(16)
C6	0.81652(44)	0.45954(34)	0.34499(32)	574(13)
C7	0.82521(60)	0.33315(39)	0.37469(41)	792(18)
C8	0.67454(76)	0.28223(50)	0.39616(87)	1815(50)
C9	0.53815(54)	0.34804(37)	0.40685(44)	706(18)
C10	0.66822(40)	0.48034(27)	0.28650(28)	469(13)
O11	0.71678(26)	0.49813(23)	0.52597(21)	652(9)
C12	0.39178(39)	0.51376(37)	0.32409(33)	581(14)
C13	0.26358(50)	0.50998(56)	0.40787(48)	897(21)
C14	0.34783(58)	0.45184(57)	0.21635(47)	975(21)
O15	0.66637(31)	0.58582(21)	0.22721(23)	600(9)
C16	0.90564(89)	0.26666(59)	0.28648(67)	1263(32)

chromator, room temperature, ω scan, learnt profile method, 2° < 2Θ < 43°, 5951 measured reflexions (whole Ewald sphere), 1488 unique reflexions (Friedel pairs separate), no absorption correction, structure solution by direct methods and difference Fourier synthesis, refinement with anisotropic temperature factors for the non-hydrogen atoms, hydrogen atoms included with some constraints, $R_w = 0.05$, $w = 1/\sigma(F)$. Programs used: STRUCSY (Stoe & Cie), SHELX-76,84 (G. M. Sheldrick), PARST (M. Nardelli), ORTEP (C. K. Johnson), SCHAKAL (E. Keller). C8 has a highly anisotropic temperature ellipsoid (cf. Figure 1b). The final difference Fourier synthesis shows a residual electron density of $0.39 \cdot 10^{-6}$ e/pm^3 near C8, i.e. hydrogen atoms H81 and H82 bonded to C8 are not well determined. The absolute structure of the molecule could not be determined, because the refinement of the inverted coordinates yielded no significant change in the *R* values. The molecules are linked by weak hydrogen bonds, O15—H151···O11′ forming chains along the *z* axis. The atomic coordinates and thermal parameters are listed in Table 1.

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[16/90]