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SYNTHESIS OF TETRACYCLO[3.3.0.0^{2,4}.0^{3,6}]OCT-7-ENE AND SOME OF ITS DERIVATIVES

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Abstract—A full account is given of the synthesis of the title compound, its 7,8-dihydro-analogue and of some of its derivatives.

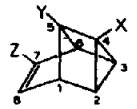
Compounds possessing the carbon skeleton of tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octane are rather scarce. Sasse and coworkers have obtained 7,8 - benztetracyclo-[3.3.0.0^{2,4}.0^{3,6}]oct - 7 - enes by photoreaction of naphthalenes with tolane.[1] In 1970 we reported the synthesis of 4 - carbomethoxytetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct - 7 - ene **1c** by quasi-Favorskii ring contraction.[2] The main product from the reaction of hexamethyl Dewar benzene and tetracyanoethylene has the structure of a *homo* Diels–Alder adduct.[3] 4 - Carbomethoxy - 5 - phenyltetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct - 7 - ene **1b** was obtained in high yield from the photochemical addition of methyl phenylpropiolate to benzene.[4]

All of the aforementioned methods produce rather specifically substituted tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct - 7 - enes. Our first attempt to prepare the parent **1a** by intramolecular carbon hydrogen insertion of 3 - carbenatricyclo[3.2.1.0^{2,4}]oct - 6 - ene failed.[5] In 1977 we succeeded in synthesizing **1a** *via* the intramolecular addition of 7-norbornadienyl carbene (**2**, R = H, X = CH) to its *syn* double bond.[6] So far, **1a** is the newest valence isomer of the $(CH)_8$ family. In the present paper we wish to give the details of the preparation of **1a** as well as to show the more general applicability of our approach, which allows the introduction of a number of substituents into **1a** yielding compounds, which we needed in labelling studies concerning the unimolecular reactions of **1a**.[7]

RESULTS

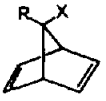
The key material for the preparation of **1a** is 7-carbomethoxynorbornadiene **2a**.[8] The conversion of **2a** to the tosylhydrazones **2b** and **2c** is described elsewhere.[8] The conditions for the intramolecular carbene addition turned out to be rather specific. Pyrolysis of the sodium salt of **2b** in diglyme gave styrene (*ca.* 10%) as the major monomeric product, whereas high vacuum flash pyrolysis produced traces of benzene, fulvene and unidentified C_8H_8 and C_8H_{10} compounds. Photolysis of the sodium salt of **2b** in THF through a Duran 50 filter at room temperature also gave mainly polymer. However, when the photolysis was carried out at low temperature six products were obtained in a total yield of *ca.* 65% (eqn 1, R = H).

The three main components are the ones expected from 7-norbornadienyl carbene: the desired carbene-olefin addition product **1a** (30–35%), the hydrogen shift product 7-methylenenorbornadiene **3a** (20–25%) and the carbon shift product barrelene **4a** (3–4%). 3-Methylenequadricyclane **5a** (2%) probably is not a primary carbene product, but is formed from **3a** as shown by an independent conversion of **3a** to **5a** under the reaction conditions. The mode of formation of traces of cyclooctatetraene **6a** and semibullvalene **7a** is unclear. The identities of compounds **3a–7a** were confirmed by comparison of their spectral properties with those of authentic samples.[9] The structure assignment of **1a** rests on its



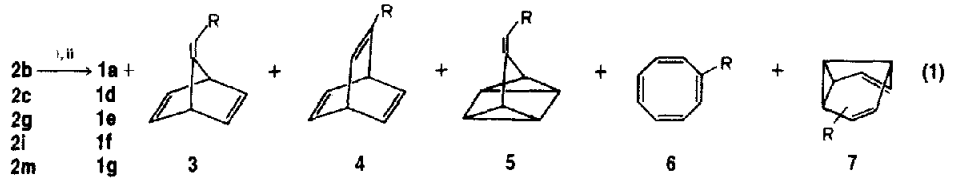
1

a: X = Y = Z = H
b: X = CO_2Me, Y = C_6H_5, Z = H
c: X = CO_2Me, Y = Z = H
d: X = D, Y = Z = H
e: X = Z = H, Y = D
f: X = Z = H, Y = Me
g: X = Z = H, Y = CO_2Me
h: X = Z = H, Y = CHO
i: X = Z = H, Y = CH_2OH
j: X = Z = H, Y = $CHNNHSO_2C_7H_7$
k: X = Z = H, Y = OH
l: X = Me, Y = Z = H
m: X = Y = H, Z = Me
n: X = Y = Me, Z = H
o: X = H, Y = Z = Me



2

a: R = H, X = CO_2Me
b: R = H, X = $CHNNHSO_2C_7H_7$
c: R = H, X = $CDNNHSO_2C_7H_7$
d: R = D, X = CO_2Me
e: R = D, X = CHO
f: R = D, X = CH_2OH
g: R = D, X = $CHNNHSO_2C_7H_7$
h: R = Me, X = CO_2Me
i: R = Me, X = $CHNNHSO_2C_7H_7$
j: R = Me, X = CH_2OH
k: R = Me, X = CHO
l: R = CHO, X = CO_2Me
m: R = $CHNNHSO_2C_7H_7$, X = CO_2Me
n: R = Cl, X = CO_2Me



i: NaH, THF, rt
ii: *hν* (Duran 50), THF, −78°

a: R = H
b: R = D
c: R = Me
d: R = CO_2Me

^1H and ^{13}C NMR spectra which both show the C_s symmetry of the molecule. The ^{13}C spectra (proton decoupled and fully coupled) show the presence of five different kinds of CH groups. According to Balaban[12] there is only one $(CH)_8$ valence isomer with one double bond, and five different kinds of carbons: **1a**. Additional proof was obtained by conversion of **1a** to tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]octane **8** and to **1c**,[2] both also prepared by independent routes (*vide infra*). The use of **2c** instead of **2b** yielded **1d** containing 98 ± 2% d_1, the deuterium being located at C-4 exclusively.

The dihydro-derivative of **1a**, **8**, could be prepared in an analogous manner: low temperature photolysis of the sodium salt of the tosylhydrazone derived from *syn* - 7 - norbornenecarbaldehyde[11] gave the three expected products (**8**, **9**, **10**) of the intermediate carbene, the hydrogen shift product **9** now dominating (eqn 2).

The identity of **9** and **10** was established by comparison of their spectral properties with those of authentic samples. The structure of **8** is derived from its ^1H and ^{13}C NMR spectra (proton decoupled and fully coupled) and by comparison of its spectral properties with those of the product obtained by diimide reduction of **1a**.

reduction of **1a**.

The strained nature of the carbon skeleton of both **1a** and **8** is reflected by the very high values of $J_{^{13}C-^1H}$ of the cyclopropyl carbons as seen by comparison with the higher homologue deltacyclene **11** (Fig. 1). We have used the resulting high acidity of H-4 to introduce substituents at C-4 of **1a** (*vide infra*).

On catalytic hydrogenation (PtO_2/EtOH) **1a** rapidly takes up three equivalents of hydrogen yielding 7-methylnorbornane as the only product. *Anti* - 7 - methylnorbornene and **8** could be detected as intermediates in this reaction. The known stability of tricyclo[3.3.0.$0^{2,7}$]octane under these conditions[13] rules out this molecule as a possible intermediate and the opening of the tricyclohexane substructure possibly involves the intermediacy of a platina carbene complex.[14] Under the same conditions **1f** yields[3] 7,7-dimethylnorborane.

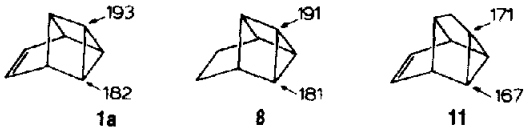
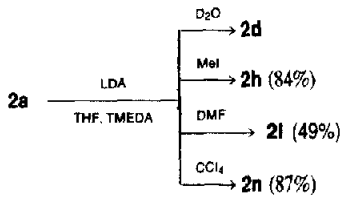


Fig. 1. Absolute values of $J_{^{13}C-^1H}$ (Hz).

Introduction of substituents at C-5 of **1a** starts with the ester **2a**: **2a** easily can be enolized and subsequent reaction with electrophiles yields 7,7-disubstituted norbornadienes (eqn 3).



(3)

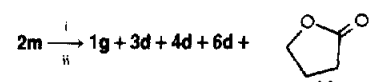
Reaction with D_2O afforded **2d** which was ultimately converted into **1e** via reduction to **2e**. **1e** Contained 89 ± 0.5% d_1 as determined by mass spectroscopy, the deuterium being located at C-5 exclusively as indicated by its ^1H NMR spectrum. Reaction with methyl iodide gave **2h** (eqn 3) from which tosylhydrazone **2i** could be prepared (77%) via reduction to the alcohol **2j** (81%) and subsequent oxidation to the aldehyde **2k** (74%). When **2i** was treated like **2b** five products were formed (eqn 4):

i: NaH, THF, rt
ii: *hν* (Duran 50), THF, −78°

(4)

In addition to the desired **1f** (31%) the carbon shift products **3c** (2%) and **4c** (8%) were obtained. Product **12** (4%) results from insertion of the carbene atom into one of the C–H bonds of the methyl group, whereas **13** (trace) probably is derived from **12** in close analogy with the formation of **5a** from **3a** (*vide supra*).

Reaction of the enolate of **2a** with DMF afforded 7 - carbomethoxy - 7 - norbornadienecarbaldehyde **2l** (eqn 3), the aldehyde function of which could be selectively converted into a tosylhydrazone: **2m** (83%). Treatment of **2m** as above gave five products (eqn 5):



(5)

i: NaH, THF, rt
ii: *hν* (Duran 50), THF, −78°

(2)

i: NaH, THF, rt
ii: *hν* (Duran 50), THF, −78°

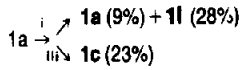
The formation of **1g** (43%), **3d** (2%), **4d** (5%) and **6d** (2%) closely parallels the pattern found in eqns (1) and (4). The origin of butyrolacton **14** (9%) is not clear.

With diisobutyl aluminium hydride,[15] **1g** was converted into aldehyde **1h** (86%) together with traces of the corresponding alcohol **1i**. Again **1h** was converted into its tosylhydrazone **1j** which served as the starting material in an attempted intramolecular carbene-olefin addition analogous to the one leading to **1a**.[16]

With carbon tetrachloride as electrophile[17] 7 - chloro - 7 - carbomethoxynorbornadiene **2n** was readily prepared (eqn 3). However, reduction of the ester function turned out not to be feasible without affecting the chlorine: all efforts, including reductions with $LiAlH_4$[18] (with and without $AlCl_3$), AlH_3,[19] DIBAH,[15] $NaBH_4$, $LiBH_4$, $Li(MeO)_3AlH$ and KH[20] under a variety of conditions gave either starting material and/or products lacking the chlorine. Not quite unexpectedly the chlorine seems to be the more reactive site of the molecule.

A related carbene approach was used to synthesize 5 - hydroxytetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct - 7 - ene **1k**. Anionized epoxides are known to undergo α - elimination to carbenes under certain conditions.[21] We therefore synthesized the epoxide **15**[22] and subjected it to anionization conditions (LDA; DEE). After one hour at room temperature hydrolysis and work-up of the reaction mixture afforded cycloöctatrienon **16**[23] as the only product (Scheme 1). As the intermediacy of **1k** seemed quite reasonable in this conversion the anionization was carried out for six hours at −30°. After aqueous work-up only one product, besides starting material, was found, tricyclo[3.2.1.0^{2,4}]oct - 6 - en - 8 - one **17**.[24] This finding strengthened our hope regarding the involvement of **1k** and therefore the same reaction was carried out for 110 hr at −60°. After work-up as above the ^{1}H NMR spectrum of the crude reaction mixture revealed the presence of starting material **15**, **17** and a new product which showed the characteristic signals of a 5-substituted tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct - 7 - ene in an approximate ratio of 2:3:1. **16** Could not be seen in the ^{1}H NMR. Glc analysis of the mixture confirmed the presence of **15** and **17**. However, **16** was also obtained instead of **1k**. With carefully chosen glc conditions **1k** could be isolated. These findings are consistent with the occurrence of a homoenolate equilibrium[25] (**18**⇄**19**) from which at higher temperatures **20** is formed irreversibly (Scheme 1). As high yields of **1k** seem to ask for inconvenient long reaction times at very low temperatures this reaction was not further optimized.

The high acidity of H-4 allowed functionalization of **1**. When **1a** was subjected to *n*-BuLi/TMEDA slow lithiation at C-4 and (to a lesser degree) C-7 took place. Reaction of the lithiation mixture with methyl iodide afforded **1l** and **1m** besides some unreacted **1a** (eqn 6). Surprisingly no indication was found of addition of the alkyllithium to the double bond.[26]

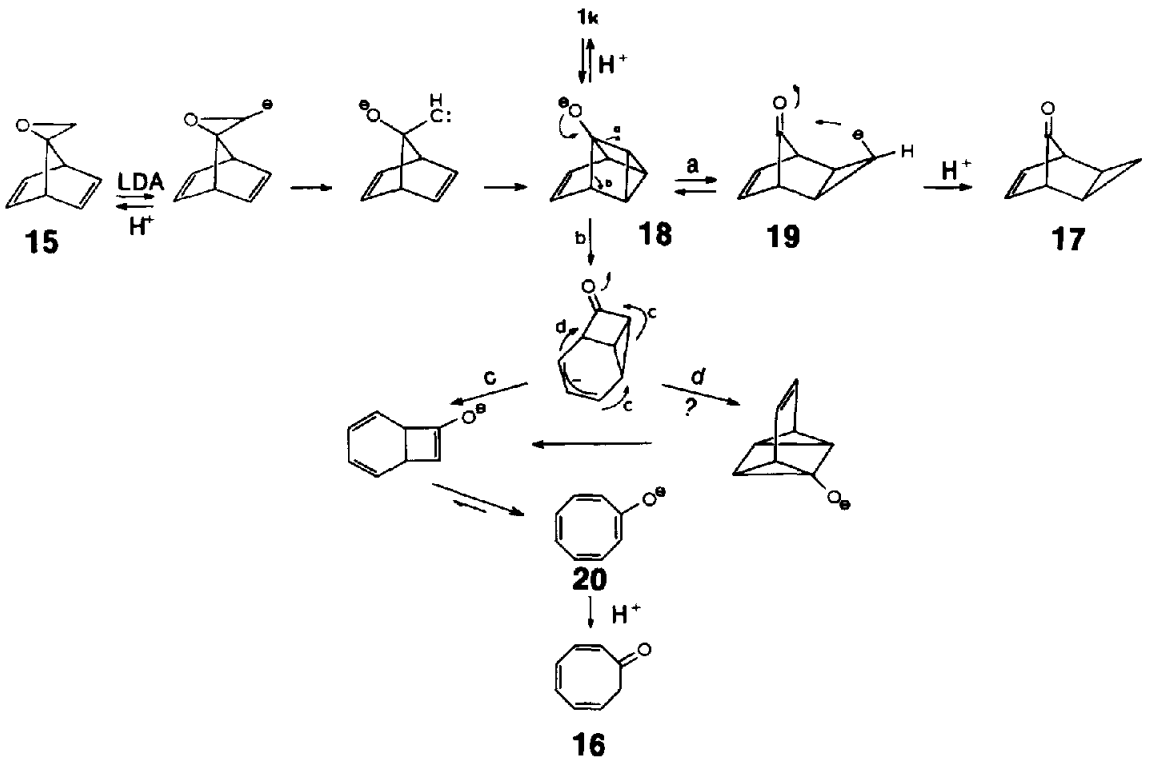


(6)

(7)

i: *n*-BuLi, TMEDA/hexane (1 : 1)
ii: MeI
iii: CO_2, H^+, CH_2N_2

Carbon dioxide quench of the lithiation mixture and acid work-up followed by esterification gave **1c** identical in all respects with **1c** prepared by our previous route[2] (eqn 7). This finding again establishes the identity of **1a**. Metallation of **1f** under comparable conditions followed by reaction with methyl iodide produced **1n** and **1o** in close analogy with the corresponding reaction of **1a** (eqn 8).



Scheme 1.

$$\mathbf{1l} \xrightarrow[ii]{i} \mathbf{1f}\ (8\%) + \mathbf{1n}\ (41\%) + \mathbf{1o}\ (3\%) \qquad (8)$$

i: *n*-BuLi, TMEDA/hexane (1:1)
ii: MeI

It is apparent that the protons in **1a** and **1f** possessing $J_{^{13}C-^{1}H}$'s greater than *ca.* 160 Hz are susceptible to metallation. When metallation occurs at the cyclopropane ring the most acidic proton (H-4) is chosen in spite of a statistical disadvantage.

The ^{13}C and ^{1}H NMR spectra of some selected compounds are summarized in Tables 1–3.

CONCLUDING REMARKS

A number of interesting compounds has become available by intramolecular addition of 7-norbornadienyl carbenes to their *syn* double bond. Tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct - 7 - ene **1a** is conveniently prepared from 7-chloronorbornadiene in a four step procedure in 17% overall yield. Enolisation of **2a** allows the introduction of various substituents at C-5 in **1**. The product pattern of the intramolecular carbene reactions shows good consistency throughout the series, though the predominant formation of tetracyclic products is somewhat surprising, as other reaction channels seem to be more favourable energetically (e.g. the formation of benzene and acetylene or the formation of 3- and 4-type products). This may be an example of the operation of the principle of least nuclear motion. The reactivity of **1a** and its derivatives is now the subject of our investigations.

EXPERIMENTAL

IR spectra were recorded as 10% solutions in CCl_4 or as KBr disks on a Perkin-Elmer 580B spectrophotometer. Only strong and medium absorptions are given (cm^{-1}) with a precision of 5 cm^{-1}. Mass spectra were obtained from a Varian Mat CH_5-DF spectrometer (70 eV). For GC/MS a Varian Aerograph 1740 was coupled to the mass spectrometer. Peak heights of fragments are given in brackets relative to the base peak (100%). Gaschromatographic analyses were performed on a Varian 90 or 920 or on an Intersmat GC 120. H_2 was used as carrier gas. The injector and detector were set at 150° unless stated otherwise. Columns (stainless steel) used: A: 15% SE-30 on Chromosorb WAW-DMCS, 60–80 mesh (0.4 × 180 cm); B: 15% Apiezon M on Chromosorb WAW-DMCS, 60–80 mesh (0.4 × 150 cm); C: 10% Carbowax 20M on Chromosorb W-HP, 80–100 mesh (0.4 × 150 cm); D: 3.8% SE-30 on Chromosorb WAW-DMCS, 60–80 mesh (0.4 × 150 cm). NMR spectra were recorded on a Bruker WH-90 or WH-400 spectrometer in $CDCl_3$ with $CHCl_3$ or $CDCl_3$ as internal standard. ^{1}H NMR spectra are 90 MHz spectra unless stated otherwise; ^{13}C NMR spectra are 22.63 MHz spectra; chemical shifts (δ_{TMS}) are given in ppm with a precision of 0.01 ppm (^{1}H) or 0.1 ppm (^{13}C); coupling constants have an accuracy of 0.3 Hz (^{1}H) or 1.5 Hz (^{13}C).[27] Only $^{1}J_{^{13}C-^{1}H}$'s are given, although many of the signals showed further splittings; those which showed no further splittings or broadening are indicated with an asterisk in Table 1. Abbreviations used: b = broad, p = pseudo, s = singulet, d = doublet, t = triplet, qa = quartet, qi = quintet, sx = sextet, m = multiplet, rrv = relative retention volume. M.ps are uncorrected. All compounds were colourless liquids unless stated otherwise. All solvents were distilled shortly before use: ethereal solvents were distilled from $LiAlH_4$ and stored over Na-wire, n-pentane was washed twice with conc H_2SO_4, twice with brine, dried over $CaCl_2$, distilled from $LiAlH_4$ and stored over Na-wire, DMSO was distilled from CaH_2 and stored over molecular sieves, DMF was dried according to Ref. 28 and stored over molecular sieves, TMEDA was dried by distillation from KOH and used immediately, and benzene was dried by distillation, discarding the first distillate, and stored over molecular sieves. All reactions were carried out in previously dried glassware in an inert atmosphere (N_2 or argon). Some of the reaction mixtures were worked up by short path evaporative distillation (MDA); temperatures given are heating bath temperatures.

Syn - 7 - *norbornenecarbaldehyde.*[32] Obtained in 39% yield by Pfitzner Moffatt oxidation[12a] of *syn* - 7 - norbornenyl methanol.[12b] The aldehyde was identical with respect to all properties with a sample prepared according to Ref. 12c. For a detailed description of the oxidation reaction: see Ref. 8.

Preparation of tosylhydrazones **2g**, **2i**, **2m** *and* **1j** *and of the tosylhydrazone of* syn - 7 - *norbornenecarbaldehyde.* Prepared according to Ref. 31. Yields: tosylhydrazone of *syn* - 7 - norbornenecarbaldehyde: 78%; **2g**: 89%; **2i**: 82%; **2m**: 83%; **1j**: 81%. ^{1}H NMR showed the tosylhydrazone of *syn* - 7 - norbornenecarbaldehyde, **2g** and **2i** to consist of a single stereoisomer (as is also the case with **2b** and **2c**). Tosylhydrazone of *syn* - 7 -

Table 1. ^{13}C chemical shifts [22.63 MHz, δ_{TMS} (ppm)] and $^{1}J_{^{13}C-^{1}H}$ (in parentheses, Hz) of some selected compounds mentioned in the text. (*): No further splittings (**): not determined due to overlap of peaks; (***): for clarity the carbon atoms of **11** have been numbered as in **1**; the CH_2 group of **11** is arranged under X/Y/Z

Compound	C_1/C_6	C_2/C_3	C_4	C_5	C_7/C_8	X/Y/Z
1a	50.5	21.0	30.3	55.7	136.6	-
	(150.0)	(182.4)	(192.7)*	(156.4)	(164.7)	-
1c	49.3	34.3	30.3	58.2	136.0	OMe: 51.2; CO_2: 172.8
1f	54.7	20.3	24.0	65.2	135.4	14.3
	(150.0)	(182.4)	(191.2)	(--)	(161.8)	(124.5)
1g	53.2	20.1	24.9	64.5	135.5	OMe: 51.3; CO_2: 179.4
	(152.2)	(183.8)	(198.5)*	(--)	(167.7)	(147.1)* (--)
1l	48.0	25.3	29.8	57.1	136.0	12.9
1n	52.9	25.0	31.8	64.2	134.6	12.3 10.3
8	46.8	17.7	22.4	47.3	29.4	-
	(**)	(180.9)	(191.0)*	(**)	(ca.129)	-
11***	48.6	22.8	26.1	57.9	135.3	32.7
	(149.4)	(167.0)	(171.4)	(145.0)	(169.9)	(128.9)*

Table 2. ^{1}H chemical shifts [90 MHz, δ_{TMS} (ppm)] and coupling constants (in parentheses, Hz) of some selected type-1 compounds mentioned in the text. ×): Hydroxy proton not found

Compound	H_1	H_6	H_2/H_3	H_4	H_5	H_7/H_8	X/Y/Z
1a	3.61 (m)	3.61 (m)	1.96 (m)	2.47 (m)	2.41 (bpqi)	6.09 (t, 1.8)	-
1d	3.61 (m)	3.61 (m)	1.96 (bd, 4.5)	-	2.41 (pqi)	6.09 (t, 1.8)	-
1e	3.61 (bs)	3.61 (bs)	1.96 (m)	2.47 (bt, 3.6)	-	6.09 (t, 1.8)	-
1f	3.14 (bs)	3.14 (bs)	1.98 (m)	2.41 (bt, 3.5)	-	6.03 (bt, 1.8)	Y: 0.80 (bs)
1g	3.85 (m)	3.85 (m)	2.07 (m)	2.94 (t, 3.5)	-	6.06 (t, 1.8)	Y: 3.67 (s)
1h	3.97 (m)	3.97 (m)	2.15 (m)	3.00 (bt, 3.8)	-	6.08 (t, 1.8)	Y: 9.35 (bs)
1i	3.47 (m)	3.47 (m)	2.07 (m)	2.62 (bt, 3.7)	-	6.04 (t, 1.8)	Y: 3.33 (bs); x
1k	3.40 (m)	3.40 (m)	2.00 (m)	2.92 (bt, 4.0)	-	6.06 (t, 1.8)	x
1l	3.52 (m)	3.52 (m)	1.77 (m)	-	2.26 (pqi)	6.06 (t, 1.8)	X: 1.38 (bs)
1m	3.53 (m)	3.43 (bd, 4.6)	2.00 (m)	2.46 (m)	2.46 (m)	H_8: 5.64 (m)	Z: 1.76 (bd, 1.5)
1n	3.07 (bs)	3.07 (bs)	1.79 (bs)	-	-	5.99 (t, 1.8)	X: 1.36 (bs); Y: 0.74 (bs)
1o	3.03 (bs)	2.91 (bs)	1.99 (m)	2.37 (bt, 3.7)	-	H_8: 5.57 (m)	Y: 0.80 (bs), Z: 1.75 (bd, 1.7)

Table 3. ^{1}H chemical shifts [90 MHz, δ_{TMS}(ppm)] and coupling constants (in parentheses, Hz) of some selected type-2 compounds mentioned in the text. ×): N–H proton not found

Compound	H_1/H_4	$H_2/H_3/H_5/H_6$	X	R
2g	3.49 (m)	6.58 (t, 2.0); 6.81 (t, 2.1)	ArH: 7.79 (m, 2H), 7.32 (m, 2H); CHN: 7.05 (s) ArMe: 2.42 (s); NH: 7.60 (bs)	-
2h	3.60 (m)	6.76 (t, 2.0); 6.64 (t, 2.1)	3.60 (s)	1.23 (s)
2i	3.37 (pqi)	6.69 (t, 2.0); 6.47 (t, 2.0)	ArH: 7.80 (m, 2H), 7.31 (m, 2H); CHN: 7.26 (s) ArMe: 2.44 (s); NH: x	1.14 (s)
2j	3.23 (pqi)	6.72 (t, 2.1); 6.68 (t, 2.1)	CH_2: 3.73 (bd, 5.6); OH: 1.12 (bt, ca. 6)	1.23 (s)
2k	3.60 (pqi)	6.80 (t, 2.1); 6.74 (t, 2.1)	9.54 (s)	1.08 (s)
2l	4.12 (pqi)	6.84 (t, 2.1); 6.77 (t, 2.1)	3.66 (s)	9.52 (s)
2n	3.91 (pqi)	6.74 (t, 2.1); 6.66 (t, 2.1)	3.69 (s)	-

norbornenecarbaldehyde: ^{1}H NMR: 1.00 (m, 2H, H - 5,6 - *endo*), 1.72 (m, 2H, H - 5,6 - *exo*), 2.34 (bd, 6.5 Hz, 1H, H-7), 2.43 (s, 3H, ArMe), 2.79 (m, 2H, H-1,4), 5.89 (bt, 1.8 Hz, 2H, H-2,3), 7.10 (d, 6.5 Hz, 1H, CHN), 7.32 (m, 3H, ArH and NH), 7.81 (m, 2H, ArH). The ^{1}H NMR spectra of **2g** and **2i** are given in Table 3. According to ^{1}H NMR **2m** and **1j** were obtained as *ca.* 10:1 **2m** and 2:1 **1j** mixtures of stereoisomers. ^{1}H NMR (**2m**, major isomer): 2.43 (s, 3H, ArMe), 3.57 (s, 3H, OMe), 3.85 (pqi, 2H, H-1,4), 6.53 (t, 2.1 Hz, 2H, H-2,3 or 5,6), 6.76 (t, 2.1 Hz, 2H, H-2,3 or 5,6), 7.15 (s, 1H, CHN), 7.31 (m, 2H, ArH), 7.40 (bs, 1H, NH), 7.76 (m, 2H, ArH); the spectrum of the minor isomer of **2m** was partly obscured by the absorptions of the major isomer and showed absorptions at 2.41, 3.54, 4.17, 6.43, 6.71 and 7.17 ppm; (**1j**, major isomer): 2.05 (m, 2H, H-2,3), 2.44 (s, 3H, ArMe) 2.83 (t, 3.6 Hz, 1H, H-4), 3.60 (m, 2H, H-1,6), 5.99 (t, 1.8 Hz, 2H, H-7,8), 6.88 (s, 1H, CHN), 7.20–7.87 (m, 4H, ArH), NH not found; (**1j**, minor isomer): 2.16 (m, 2H, H-2,3), 2.44 (s, 3H, ArMe), 2.86 (t, 3.8 Hz, 1H, H-4), 3.68 (m, 2H, H-1,6), 6.29 (t, 1.8 Hz, 2H, H-7,8), 6.49 (s, 1H, CHN), 7.20–7.87 (m, 4H, ArH), NH not found. No attempt was made to separate the isomers. All compounds: white solids; m.p.'s: tosylhydrazone of *syn* - 7 - norbornenecarbaldehyde: 121–123.5° (dec.); **2g**: 135–136° (dec.); **2i**: 79–81.5°; **2m**: 124–125°; **1j**: 125° (dec.). IR (**2i**, KBr): 3200, 1596, 1360, 1338, 1303, 1291, 1162, 1091, 1043, 813, 740, 658, 602, 550; (**2m**, KBr): 3180, 1738, 1433, 1358, 1297, 1271, 1203, 1166, 1149, 1018, 816, 746, 670, 565, 548, 516; (**1j**, KBr): 3215, 1595, 1438, 1360, 1330, 1313, 1186, 1161, 997, 816, 739, 711, 667, 652, 571, 548.

Preparation of the sodium salts of **2b**, **2c**, **2g**, **2i** *and of the tosylhydrazone of* syn - 7 - *norbornenecarbaldehyde and subsequent photolysis.* 4.5 mmol NaH (55–60% dispersion in oil) was washed twice with dry *n*-pentane. The solvent was removed and 45 ml dry THF was added. The resulting suspension was cooled to 0° and within 5 min a solution of 4.5 mmol tosylhydrazone in 45 ml dry THF was added dropwise with magnetic stirring. After wrapping the vessel with aluminum foil the mixture was allowed to warm to room temp and to react for an additional 2 hr. With the aid of an additional amount of 360 ml dry THF the resulting suspension or soln was then transferred into the photolysis apparatus which is essentially equal to the one described in Ref. 29. The mixture was cooled in dry ice/*i*-PrOH for 30 min and then photolyzed for 5 hr at −78° (400 W medium pressure Hg; Applied Photophysics Ltd, 400 LQ; Duran 50 filter). After warming to room temp the mixture was diluted with 500 ml *n*-pentane and washed first with 10 portions of 500 ml H_2O, then twice with 100 ml brine and dried ($MgSO_4$). After filtration the mixture was carefully concentrated through a 20 cm vacuum-jacketed vigreux column. The remaining volatile components were then collected under reduced pressure (*ca.* 1 torr) in a trap cooled at −196°. The contents of the cold trap were subjected to preparative glc. The exact conditions are described below.

Tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1a**. The photolysis mixture obtained as above was separated by glc (B, 76°) affording variable amounts of toluene[30] (rrv: 0.58), *ca.* 105 mg (*ca.* 1.0 mmol, 20–25%) **3a** (rrv: 0.68), *ca.* 168 mg **1a** + **4a** (rrv: 1.00), traces of **6a** + **7a** (rrv: 1.26) and 9 mg (0.1 mmol, 2%) **5a** (rrv: 1.51). The mixture of **1a** + **4a** was separated on column C (60°) yielding *ca.* 152 mg (*ca.* 1.5 mmol, 30–35%) **1a** (rrv: 1.00) and *ca.* 16 mg (*ca.* 0.2 mmol, 3–4%) **4a** (rrv: 1.72). All other samples gave single peaks under these conditions. All compounds except **1a** were identified by comparison of their spectral data with those of authentic samples.[9] The ^{13}C and ^{1}H NMR spectra of **1a** are given in Tables 1 and 2. Its IR spectrum is reported elsewhere.[5] Calc. for C_8H_8: 104.0626; found: 104.0624; *m/e*: 104 (66), 103 (94), 102 (22), 78 (100), 77 (53). When **3a** was re-subjected to the photolysis conditions described above *ca.* 3% **5a** was formed.

Tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* - 4 - d **1d**. After reaction as above **2c** afforded **1d** containing 98 ± 2% d_1, as indicated by mass spectrometry. Its ^{1}H NMR spectrum is given in Table 2. In **3b** and **4b** the deuterium was found at the positions indicated in eqn (1) exclusively, as determined by ^{1}H NMR. The positions of deuterium in **5b** and **7b** were not determined.

Tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* - 5 - d **1e**. After reaction as above **2g** afforded **1e** containing 89.0 ± 0.5% d_1, as indicated by mass spectrometry. Its ^{1}H NMR spectrum is given in Table 2. In **3b** and **4b** the deuterium was found at the positions indicated in eqn (1) exclusively, as determined by ^{1}H NMR. The positions of deuterium in **5b** and **7b** were not determined.

Diimide reduction of tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1a**. To a magnetically stirred mixture of 91.9 μl 96% EtOH, 99.6 μl $N_2H_4 \cdot H_2O$ and 27.5 mg (0.26 mmol) **1a** at 0° 16.7 μl 1% $CuSO_4/H_2O$ was added. Then 54.6 μl 30% H_2O_2 was added slowly (25 min) with a syringe. After the addition was complete the mixture was stirred for an additional 5 min. The mixture was then diluted with 35 ml *n*-pentane and washed first 3 times with 15 ml H_2O, then once with 15 ml brine and dried over $MgSO_4$. After careful concentration at 760 torr with a 20 cm vacuum jacketed vigreux the crude residue was subjected to preparative glc (B, 62°) to afford 10.0 mg (36% recovery) **1a** (rrv: 1.00) and 11.5 mg (0.11 mmol, 65%) **8** (rrv: 1.28). **8** Obtained in this way was identical in all respects with **8** prepared from the tosylhydrazone of *syn* - 7 - norbornenecarbaldehyde (*vide infra*).

Tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]*octane* **8**. The photolysis mixture from the sodium salt of 622.3 mg (2.1 mmol) of the tosylhydrazone of *syn* - 7 - norbornenecarbaldehyde obtained as described above was separated by glc (B, 63°) affording toluene[30] (rrv: 0.50), 53.1 mg (0.5 mmol, 23%) **9** (rrv: 0.58) and 38.9 mg **8** + **10**. The mixture of **8** and **10** was separated on column C (60°) yielding 30.7 mg (0.3 mmol, 14%) **8** (rrv: 1.00) and 8.2 mg (0.1 mmol, 4%) **10** (rrv: 1.60). **9** Gave a single peak under these glc conditions. Besides these three expected products 3% 3-methylenenortricyclane (B, 63°: rrv: 0.74) was found, probably originating from impurities in the tosylhydrazone. The identity of **9**, **10** and 3-methylenenortricyclane was confirmed by comparison of their spectral data with those of authentic samples. The ^{13}C NMR spectrum of **8** is given in Table 1; ^{1}H NMR (90 MHz): 1.15–1.87 (m, 6H, H-2,3,7,8), 2.46 (m, 2H, H-4,5), 3.07 (m, 2H, H-1,6); ^{1}H NMR (400 MHz): 1.34 (m, 2H, H-7,8-*endo*), 1.59 (m, 2H, H-2,3), 1.71 (m, 2H, H-7,8-*exo*), 2.42 (dt, 3.5 Hz, 0.8 Hz, 1H, H-4), 2.46 (pqi, 1H, H-5), 3.07 (m, 2H, H-1,6); IR (CCl_4): 3060, 3000, 2955, 2900, 2865, 1310, 1247, 1236, 1214, 1148, 1051; calculated for C_8H_{10}: 106.0782; found: 106.0779; *m/e*: 106 (17), 105 (31), 103 (12), 91 (78), 79 (40), 78 (100). **8** Obtained in this reaction was identical in all respects with **8** from the diimide reduction of **1a**.

Catalytic hydrogenation of tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1a** *and* 5 - *methyltetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1f**. A spatula tip of PtO_2 was prehydrogenated for 5 min in 1 ml 96% EtOH. To this mixture 7.7 mg (0.074 mmol) **1a** in 25 μl 96% EtOH was added with a syringe. Vigorous magnetic stirring at 22° caused the rapid uptake of 4.75 ml (0.21 mmol; 2.9 equiv.) H_2. The H_2 uptake stopped after 5 min. The mixture was then diluted with 10 ml *n*-pentane, filtered, washed 5 times with 5 ml H_2O, once with 5 ml brine and dried over $MgSO_4$. Careful concentration through a 20 cm vacuum jacketed vigreux and preparative glc (D, 54°) of the crude mixture afforded 5.7 mg (0.052 mmol, 70%) 7-methylnorbornane as the only product. The identity of 7-methylnorbornane was confirmed by comparison of its spectral data with those of an authentic sample. When the reaction was stopped after 60 sec (uptake of 1.25 equiv. H_2) work-up as above gave *ca.* 3% *anti* - 7 - methylnorbornene (rrv: 0.75), 19% 7-methylnorbornane (rrv: 1.00) and 51% **8** (rrv: 1.18). The identity of *anti* - 7 - methylnorbornene was derived from its spectral data.

An analogous reduction of 7.2 mg (0.061 mmol) **1f** at 21° caused the uptake of 4.30 ml H_2 (3.1 equiv.) within 5 min. Work-up as above and preparative glc (A, 85°) of the crude mixture afforded 5.9 mg (0.048 mmol, 78%) 7,7-dimethylnorbornane (rrv: 1.00) in addition to 7% of an unidentified compound (white solid; rrv: 0.85; *m/e*: 122). The identity of 7,7-dimethylnorbornane (white solid; m.p.: 92.5–93.5°; ^{1}H NMR: 0.97 (s, 6H, Me), 1.15 (m, 4H, H - 2,3,5,6 - *endo*), 1.51 (m, 2H, H-1,4), 1.76 (m, 4H, H - 2,3,5,6 - *exo*): IR (CCl_4): 2987, 2958, 2937, 2880, 1470, 1454; calc. for C_9H_{16}: 124.1258; found: 124.1252; *m/e*: 124 (8), 109 (16), 96 (9), 82 (58), 81 (100)) was derived from its spectral data.

7 - *Carbomethoxynorbornadiene* - 7 - d **2d**. To a magnetically stirred solution of 2.6 g diisopropylamine in 25 ml dry THF at 0° 15.3 ml 1.5 *M* *n*-BuLi/*n*-hexane was added dropwise. The mixture was stirred at 0° for 15 min and cooled to −60°, at which temperature 2.00 g (13.3 mmol) **2a** in 25 ml dry THF was added, followed by the addition of 20 ml anhydrous TMEDA. The

mixture was allowed to warm to ~20° and stirred at that temperature for 1 hr. 4 ml D_2O was added and, after warming to room temperature 50 ml H_2O was added. The mixture was extracted 3 times with 100 ml ether. The combined ethereal extracts were washed 3 times with portions of 50 ml 2 *M* HCl, 3 times with portions of 100 ml brine and dried over $MgSO_4$. The mixture was concentrated at 760 torr. A sample of the residue was shown by glc and ^{1}H NMR to contain *ca.* 78% d_1 at C-7. Therefore the residue was subjected once more to the metallation conditions described above. Work-up as above followed by MDA distillation (16 torr, 90–110°) afforded 1.61 g of a colourless distillate. GLC analysis showed the presence of 80% **2d** in addition to 20% of a yet unidentified ester. Yield **2d**: 64%. **2d** Contained 90.4 ± 0.5% d_1, as determined by mass spectrometry, the deuterium being located at C-7 exclusively as indicated by its ^{1}H NMR spectrum. The origin and identity of the unidentified ester are still under investigation. The distillate was used in the subsequent reduction without further separation.

7 - (7 - *Deuterionorbornadiene)carbaldehyde* **2e**. To a magnetically stirred solution of 1.61 g **2d** (mixture, *vide supra*) in 60 ml dry ether at −55° 21.4 ml (21.1 mmol) of a commercial DIBAH/*n*-hexane solution was added slowly. After 1 hr at −55° the mixture was hydrolysed with 50 ml saturated NH_4Cl solution, warmed to room temperature and poured into a separatory funnel. The organic layer was separated; the aqueous layer was extracted 4 times with 50 ml ether. The combined organic layers were dried over $MgSO_4$ and concentrated at 760 torr. The residue was MDA distilled (10 torr, 80–100°). Preparative glc (C, 125°) afforded *ca.* 34% **2e** in addition to *ca.* 19% of the alcohol **2f**. **2e** and **2f** showed *ca.* 90% deuterium incorporation as indicated by NMR spectroscopy, the deuterium being located at C7 exclusively in both compounds. This route to **2e** is less convenient than the synthesis described in Ref. 8.

7 - *Methyl* - 7 - *carbomethoxynorbornadiene* **2h**. To a magnetically stirred solution of 3.05 g diisopropylamine in 30 ml dry THF at 0° 17.5 ml 1.6 *M* *n*-BuLi/*n*-hexane was added in 15 min. The resulting mixture was cooled to −78° and 1.50 g (10.0 mmol) **2a** in 15 ml dry THF was added dropwise in 15 min. In 10 min 30 ml anhydrous TMEDA was added. After the addition was complete the mixture was allowed to warm to −15° and was kept at that temperature for 1 hr. Then 3.0 ml MeI was added dropwise. The mixture was then allowed to warm to room temperature and stirred for 1 hr. The reaction mixture was then poured on 250 ml H_2O. The organic layer was separated and the aqueous layer was extracted with 3 portions of 75 ml ether. The combined organic layers were washed once with 75 ml brine, once with 75 ml 2 *M* HCl and again with 75 ml brine and dried over $MgSO_4$. After concentration with a rotary evaporator (760 torr, 80°) the residue was MDA-distilled (10 torr, 90°) to afford 1.38 g (8.4 mmol, 84%) colourless distillate. Glc (A, 109°) showed the presence of a single component, with no starting material detectable. The ^{1}H NMR spectrum of **2h** is given in Table 3. IR (CCl_4): 3075, 3000, 2955, 2935, 1738, 1550, 1455, 1435, 1370, 1310, 1300, 1285, 1231, 1200, 1120, 1108, 991, 881, 878, 664. *M/e*: 164 (6), 132 (100), 105 (99), 104 (77), 103 (54), 79 (51), 78 (46), 77 (79), 51 (32).

7 - (7 - *Methylnorbornadienyl)methanol* **2j**. To a stirred suspension of 380 mg $LiAlH_4$ in 50 ml anhydrous ether 1100 mg (6.7 mmol) **2h** in 8 ml dry ether was added. The resulting mixture was stirred overnight. The excess $LiAlH_4$ was carefully destroyed with H_2O. The ethereal layer was filtered, washed twice with 25 ml brine and dried over $MgSO_4$. The mixture was concentrated with a rotary evaporator (760 torr, 80°) and the residue was MDA-distilled (10 torr, 80°). The white sublimate was recrystallized from *n*-pentane at −40° to afford 757 mg (5.6 mmol, 83%) colourless needles, m.p. 85°, Glc (A, 114°) showed the presence of a single component. The ^{1}H NMR of **2j** is given in Table 3. IR (CCl_4): 3640, 3600–3200, 3075, 2975, 2935, 2880, 1547, 1308, 1023, 650. *M/e*: 136 (6), 118 (24), 117 (30), 105 (79), 93 (33), 92 (100), 91 (71), 79 (50), 77 (64).

7 - (7 - *Methylnorbornadiene)carbaldehyde* **2k**.[32] Prepared by Pfitzner Moffatt oxidation[12a] of **2j**. For a detailed description of the oxidation reaction: see Ref. 8. After MDA distillation (10 torr, 80°) a 74% yield of white crystals was obtained, m.p. 54.5–55.5°. Glc (A, 110°) showed these crystals to be *ca.* 95% pure. These crystals were used for the preparation of **2i** without further purification. The ^{1}H NMR spectrum of **2k** is given in Table 3. IR (CCl_4): 3075, 2995, 2980, 2930, 2885, 2800, 2700, 1724, 1451, 1304, 907, 680, 653. *M/e*: 134 (33), 133 (24), 119 (24), 105 (100), 91 (51), 79 (52), 77 (46).

7 - (7 - *Carbomethoxynorbornadiene)carbaldehyde* **21**.[32] To a magnetically stirred solution of 8.1 g diisopropylamine in 75 ml dry THF at 0° 50 ml 1.5 *M* *n*-BuLi/*n*-hexane was added slowly. After 15 min at 0° the mixture was cooled to −50° and 6.0 g (40 mmol) **2a** in 79 ml anhydrous THF was added dropwise, followed by the addition of 100 ml dry TMEDA. The resulting mixture was allowed to warm to −20° and to stir for 2 hr. After cooling to −30° 15 ml dry DMF was added. After 1 hr stirring at −20° the mixture was stored at −25° overnight. After adding 200 ml H_2O the mixture was allowed to warm to room temperature. After 3 extractions with ether the organic layer was washed once with brine, twice with 2 *M* HCl and again twice with brine and dried over $MgSO_4$. The mixture was concentrated at 760 torr and the residue was distilled (3 torr). The fraction boiling at 61° was collected and gave 3.5 g (19.7 mmol, 49%) of a white solid, m.p.: 24.5–25.5°. Glc (A, 130°) showed the presence of a single component. The ^{1}H NMR spectrum of **21** is given in Table 3. IR (CCl_4): 3080, 3005, 2955, 2845, 2820, 2715, 1752, 1739, 1720, 1433, 1302, 1270, 1230, 1200, 1082, 658, 646. *M/e*: 178 (2), 163 (2), 150 (16), 149 (33), 147 (10), 146 (50), 119 (47), 118 (90), 91 (100), 90 (84), 89 (52).

7 - *Chloro* - 7 - *carbomethoxynorbornadiene* **2n**. To a magnetically stirred solution of 6.06 g diisopropylamine in 60 ml dry THF at 0° 35 ml 1.5 *M* *n*-BuLi/*n*-hexane was added dropwise. After 15 min at 0° the mixture was cooled to −70° and 3.00 g (20 mmol) **2a** in 40 ml anhydrous THF was added slowly, followed by 60 ml dry TMEDA. After 1 hr stirring at −15° the mixture was cooled to −70° and 8 ml CCl_4 was added. The mixture was allowed to stand at −25° overnight. To the resulting black reaction mixture 20 ml H_2O was added, and the total was poured into 150 ml H_2O. After 3 extractions with ether the organic layer was washed twice with brine, twice with 2 *M* HCl and again with brine and dried over $MgSO_4$. After concentration at 760 torr the residue was MDA-distilled twice (10 torr, 100° and 3 torr, 60°) to afford 3.20 g (17.3 mmol, 87%) of a pale-yellow solid, m.p.: 42–43°. Glc (A, 140°) showed the presence of a single component. The ^{1}H NMR spectrum of **2n** is reported in Table 3. IR (CCl): 3085, 3020, 2958, 1750, 1438, 1312, 1300, 1280, 1262, 1225, 1197, 1063, 1049, 896, 712, 653. Calc. for $C_9H_9O_2Cl$: 184.0291; found: 184.0300. *M/e*: 186 (3), 184 (9), 152 (67), 149 (23), 125 (50), 105 (44), 91 (50), 89 (100), 77 (83), 63 (94).

5 - *Methyltetracyclo*[3.3.0.0^{2,4}.0^{3,6}]*oct* - 7 - *ene* **1i**. The photolysis mixture of 1406.1 mg (4.7 mmol) **2i** obtained as described above was analyzed by GLC (A, 62°) affording toluene[30] (rrv: 0.44), 202.5 mg **1f** + **12** (rrv: 1.00), 45.5 mg (0.4 mmol, 8%) **4c** (rrv: 1.41), 9.7 mg (0.1 mmol, 2%) **3c** (rrv: 1.47) and traces of **13** (rrv: 1.94); **5c**, **6c** and **7c** were not detected. Under the conditions given **3c** and **4c** could only be separated by repeated glc treatment. The mixture of **1f** and **12** was separated on column C (55°) yielding 171.5 mg (1.5 mmol, 31%) **1f** (rrv: 1.00) and 24.6 mg (0.2 mmol, 4%) **12** (rrv: 1.44); under these conditions all other components showed single peaks. The ^{13}C and ^{1}H NMR spectra of **1f** are shown in Tables 1 and 2; IR (CCl_4): 3060, 2965, 2920, 2865, 1445, 1337, 1110, 900, 718, 659; calc. for C_9H_{10}: 118.0782; found: 118.0783. *M/e*: 118 (33), 117 (100), 115 (45), 103 (38), 91 (39), 78 (55). The identity of **12** was confirmed by comparison of its spectral data with those of an authentic sample. **4c** (^{1}H NMR: 1.91 (d, 1.8 Hz, 3H, CH_3), 4.47 (m, 1H, H-1), 4.70 (m, 1H, H-4), 6.21 (m, 1H, H-3), 6.81 (dd, 2.6 Hz, 2.7 Hz, 4H, H-5,6,7,8); IR (CCl_4): 3070, 2980, 1579, 1326, 1218, 699, 682, 665, 642; *m/e*: 118 (60), 117 (100), 115 (38), 103 (30), 91 (48), 78 (30), 40 (80)), **3c** (^{1}H NMR: 1.47 (d, 6.7 Hz, 3H, CH_3), 3.85 (m, 1H, H-1 or H-4), 4.07, (bqa, 6.7 Hz, 1H, H-8), 4.15 (m, 1H, H-1 or H-4), 6.90 (m, 4H, H-2,3,5,6); IR (CCl_4): 3070, 3002, 2945, 2925, 2865, 1718, 1325, 709, 627; *m/e*: 118 (20), 117 (56), 115 (27), 78 (12), 40 (100)) and **13** (^{1}H NMR: 0.87 (s superimposed on m, 6H, cyclopropyl-H + H-2,4), 1.71 (m, 4H, H-1,5,6,7); IR (CCl_4): 3075, 3005, 1234, 912; *m/e*: 118 (27), 117 (100), 115 (40), 91 (54), 90 (53), 89 (37), 78 (24))

were identified on the basis of their spectral data. Low yields of C_9H_{12} compounds were also detected in this reaction; as this is always the case when the tosylhydrazones are not recrystallized before use, no attention was paid to these compounds.

5 - *Carbomethoxytetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1g**. To a magnetically stirred solution of 3.01 g (8.7 mmol) **2m** in 85 ml dry THF a suspension of 203 mg (8.5 mmol) NaH (353 mg 55–60% dispersion in oil; 3 times washed with dry *n*-pentane) in 85 ml dry THF was added dropwise at 0°. The resulting mixture was allowed to come to room temperature and stirred overnight. The white suspension was then transferred into the photolysis apparatus with the aid of 280 ml anhydrous THF, cooled in dry-ice/*i*-PrOH for 30 min and photolyzed for 5 hr at −78°. The mixture was then allowed to warm to room temperature, dried over $MgSO_4$, filtered and concentrated to *ca.* 100 ml at 760 torr. The residue was diluted with 200 ml ether, washed 3 times with brine and dried over $MgSO_4$. Further concentration and MDA distillation (4 torr, 95°) afforded 1.85 g yellow distillate. The distillate was subjected to preparative glc (A, 125°) afforded 68 mg (0.8 mmol, 9%) **1l** (rrv: 0.20), 594 mg (3.7 mmol, 43%) **1g** (rrv: 1.00), 25 mg (0.2 mmol, 2%) **3d** (rrv: 1.35), 75 mg (0.5 mmol, 5%) **4d** (rrv: 1.47) and 25 mg (0.2 mmol, 2%) **6d** (yellow liquid; rrv: 1.76). The identity of **1l** was confirmed by comparison of its spectral data with those of an authentic sample; the IR spectrum of **6d** (^{1}H NMR: 3.71 (s, 3H, OCH_3), 5.92 (m, 7H); *m/e*: 162 (18), 103 (100), 102 (60), 77 (74), 51 (56)) fitted with the one given in the literature.[33] The ^{13}C and ^{1}H NMR spectra of **1g** are given in Tables 1 and 2; IR (CCl_4): 3060, 2995, 2955, 1732, 1435, 1341, 1241, 1193, 1172, 1097, 1082, 714. Calc. for $C_{10}H_{10}O_2$: 162.0681; found: 162.0693. *M/e*: 162 (−), 103 (100), 102 (49), 78 (43), 77 (70), 51 (47). The identities of **3d** (^{1}H NMR: 3.66 (s, 3H, OMe), 3.82 (m, 1H, H-4), 4.61 (bd, 0.6 Hz, 1H, H-8), 4.89 (m, 1H, H-1), 6.88 (t, 2.1 Hz, 4H, H-2,3,5,6); IR (CCl_4): 3005, 2955, 2745, 1720, 1676, 1540, 1435, 1346, 1300, 1270, 1194, 1175, 1090, 1021, 915, 846, 689, 646; *m/e*: 162 (12), 161 (22), 131 (97), 104 (69), 103 (62), 91 (33), 77 (100), 51 (86)) and **4d** (^{1}H NMR: 3.72 (s, 3H, OMe), 4.90 (m, 1H, H-4), 5.29 (m, 1H, H-1), 6.82 (m, 4H, H-5,6,7,8), 7.59 (dd, 1.8 Hz, 5.9 Hz, 1H, H-3); IR (CCl_4): 3080, 3000, 2955, 1713, 1591, 1437, 1332, 1310, 1297, 1245, 1230, 1220, 1117, 1081, 840, 700, 642; *m/e*: 162 (20), 103 (100), 102 (53), 77 (76), 51 (58)) are derived from their spectral data.

5 - *Tetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene carbaldehyde* **1h**.[32] To a magnetically stirred solution of 565 mg (3.5 mmol) **1g** in 20 ml anhydrous ether at −70° 4 ml (4 mmol) of commercial DIBAH/*n*-hexane solution was slowly added. After 1 hr at −70° 100 ml saturated NH_4Cl solution was added. After warming to room temperature the mixture was extracted 3 times with ether and dried over $MgSO_4$. Concentration at 760 torr and MDA-distillation (14 torr, 70–90°) afforded 395 mg (3.0 mmol, 86%) colourless liquid, which was shown by glc (A, 115°) to be at least 97% pure. Traces of starting material **1g** and of the alcohol **1i** were the only impurities. Rrv: **1h**: 1.00; **1i**: 1.30; **1g**: 1.89. The ^{1}H NMR spectra of **1h** and **1i** are shown in Table 2. IR (**1h**, CCl_4): 3065, 2980, 2810, 2735, 1706, 1388, 1332, 1147, 1128, 697; (**1i**, CCl_4): 3630, 3580–3140, 3060, 2975, 2865, 1337, 1148, 1123, 1012, 720, 710, 664. Calc. for C_9H_8O: 132.0575; found: 132.0576; *m/e* **1h**: 132 (5), 131 (10), 104 (46), 103 (100), 78 (68), 77 (88); calc. for $C_9H_{10}O$: 134.0731; found: 134.0724; *m/e* **1i**: 134 (2), 133 (16), 115 (25), 103 (53), 91 (32), 78 (100).

5 - *Hydroxytetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1k**. To a magnetically stirred solution of 131 mg (1.30 mmol) diisopropylamine in 4 ml anhydrous ether at −65°, 0.81 ml 1.6 *M* *n*-BuLi/*n*-hexane was added slowly with a syringe. After 15 min at −65° the mixture was allowed to warm to room temperature, stirred at that temperature for 30 min and cooled to −65°, at which temperature 62.5 mg (0.52 mmol) **1l** was added with a syringe. After 15 min at −65° the mixture was allowed to warm to room temperature and stirred at that temperature for 1 hr. After the addition of H_2O the mixture was acidified and extracted 5 times with ether. The combined ethereal extracts were washed with brine until neutral, dried over $MgSO_4$ and concentrated at 760 torr. The residue was MDA-distilled (10 torr, 50–70°) and the distillate was analyzed by glc (A, 95°) to afford a single peak. The identity of this product, cyclooctatrienone **1o**, was established by comparison of its spectral data with those reported in the literature.[23] An analogous metallation of **1l** for 6 hr at −30° afforded a *ca.* 1:10 mixture of **1l** (rrv: 1.00) and **1j** (rrv: 1.36). The identity of **1j** was established by comparison of its spectral data with those reported in the literature.[24] When the reaction was carried out as above (the epoxide now being added in 2 ml THF) for 110 hr at −60° the ^{1}H NMR of the distillate revealed the presence of a 5-substituted tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct - 7 - ene in addition to the signals of **1l** and **1j** (*ca.* 1:2:3); no **1o** could be seen. However, when the distillate was subjected to the glc conditions described above **1l** (rrv: 1.00), **1j** (rrv: 1.36) and **1o** (rrv: 2.60) were found in the same ratio. **1k** could be purified by glc (A, 90°) when the temperature of the injector and detector was lowered to 100° and 120° respectively: **1l** (rrv: 1.00), **1j** (rrv: 1.39) and **1k** (rrv: 1.82). The ^{1}H NMR spectrum of **1k** is given in Table 2. IR (CCl_4): 3605, 3550–3160, 3065, 2980, 1338, 1220, 887, 718, 674.

4 - *Methyltetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1l** *and* 7 - *methyltetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1m**. To a magnetically stirred solution of 2.00 ml 1.6 *M* *n*-BuLi/*n*-hexane and 2.00 ml dry TMEDA 37.5 mg (0.36 mmol) **1a** in 300 μl dry *n*-pentane was added with a syringe. The mixture was stirred for 40.5 hr at room temperature. In 1 hr, 600 μl MeI was added very carefully. With the aid of 30 ml *n*-pentane and 50 ml H_2O the mixture was transferred into a separatory funnel. The aqueous layer was separated and extracted once with 30 ml *n*-pentane. The combined organic layers were extracted 3 times with 30 ml 2 *M* HCl, once with 30 ml H_2O, once with 150 ml H_2O, once with 50 ml brine and dried over $MgSO_4$. The mixture was carefully concentrated through a 20 cm vacuum jacketed vigreux column. The yellow residue was connected to a trap cooled to −196° and the volatile components were collected there under reduced pressure (1.5×10^{-2} torr). The contents of the cold trap were subjected to preparative glc (A, 60°) affording 3.3 mg (9% recovery) **1a** (rrv: 1.00), 10.8 mg (0.09 mmol, 28%) **1l** (rrv: 1.36) and 0.7 mg (0.01 mmol, 2%) **1m** (rrv: 1.83). All components showed single peaks on glc analysis on column C (60°). No products resulting from addition of *n*-BuLi to **1a** could be detected by mass spectroscopy neither in the crude mixture nor in the distillate. The ^{13}C NMR spectrum of **1l** and the ^{1}H NMR spectra of **1l** and **1m** are given in Tables 1 and 2. IR (**1l**, CCl_4): 3060, 2984, 2955, 2925, 2863, 1334, 1216, 883, 874, 715, 685; (**1m**, CCl_4): 3065, 2965, 1444, 1253, 1220, 1196, 875. *M/e* **1l**: 118 (7), 117 (65), 115 (27), 103 (37), 91 (69), 78 (69), 77 (48), 43 (100); **1m**: 118 (12), 117 (100), 115 (42), 103 (40), 91 (71), 78 (31), 77 (27).

4 - *Carbomethoxytetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1c**. A metallation of 35.8 mg (0.34 mmol) **1a** analogous to the one described in the synthesis of **1l** and **1m** was carried out for 43 hr. The mixture was poured on dry ice with the aid of a syringe. The resulting slurry was allowed to warm to room temperature and transferred into a separatory funnel with the aid of 100 ml 2 *M* NaOH and 100 ml ether. The organic layer was separated and the aqueous layer was extracted 3 times with 100 ml ether. The aqueous layer was then carefully acidified with 2 *M* HCl (pH = 2) and extracted 5 times with 100 ml ether. The combined ethereal extracts were washed once with 25 ml 2 *M* HCl, once with 25 ml brine and dried over $MgSO_4$. The mixture was concentrated on a rotary evaporator (760 torr, 55°) and the residue was treated with an excess of ethereal CH_2N_2 solution at 0°. After 1 hr the mixture was concentrated at 0° (*ca.* 15 torr) to *ca.* 10 ml. The residue was washed once with 10 ml H_2O, once with 10 ml brine and dried over $MgSO_4$. Concentration on a rotary evaporator (760 torr, 55°) left a brown residue which was subjected to preparative glc (A, 122°) to afford 12.9 mg (0.08 mmol, 23%) **1c**. The **1c** obtained this way was identical in all respects with **1c** obtained according to Ref. 2. Its ^{13}C NMR spectrum is given in Table 1. Calc. for $C_{10}H_{10}O_2$: 162.0681; found: 162.0687; *m/e*: 162 (1), 147 (10), 103 (100), 102 (46), 78 (20), 77 (41).

4,5 - *Dimethyltetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1n** *and* 5,7 - *dimethyltetracyclo*[3.3.0.$0^{2,4}$.$0^{3,6}$]*oct* - 7 - *ene* **1o**. A metallation of 41.5 mg (0.35 mmol) **1f** analogous to the one described in the synthesis of **1l** and **1m** and subsequent reaction with MeI yielded on glc analysis (A, 62°) 3 components: 3.3 mg (8% recovery) **1f** (rrv: 1.00), 17.4 mg (0.13 mmol, 41%) **1n** (rrv: 1.43) and 1.1 mg

(0.01 mmol, 3%) **1o** (rrv: 1.71). Only traces of addition products of *n*-BuLi to **1f** were detected by mass spectrometric analysis of the crude reaction mixture. The ^{13}C NMR spectrum of **1n** and the ^{1}H NMR spectra of **1n** and **1o** are given in Tables 1 and 2. IR **1n**, (CCl_4): 3058, 2960, 2920, 2862, 1445, 1334, 885, 703; **1o**, (CCl_4): 3060, 2960, 2920, 2860, 1444, 1375, 901. **1n**: calculated for $C_{10}H_{12}$: 132.0939; found: 132.0938; *m/e*: 132 (8), 131 (23), 117 (100), 116 (22), 115 (55), 91 (71), 78 (87), 77 (23); **1o**: calc. for $C_{10}H_{12}$: 132.0939; found: 132.0838; *m/e*: 132 (7), 131 (15), 117 (75), 116 (17), 115 (44), 92 (45), 91 (100).

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