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Ene Reactions of Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene

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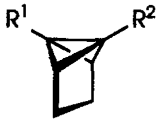
Abstract:

1,6-Dibromotricyclo[3.1.0.0^{2,6}]hexane **2e** has been prepared in 56% yield by reaction of 1,6-dilithiotricyclo[3.1.0.0^{2,6}]hexane **2d** with 2.5 equiv. of tosyl bromide. **2e** proved to be a new source for generating tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene **1** by reaction with magnesium, with lithium sand, or with *tert*-butyllithium, as shown by formation of the Diels-Alder adduct **5**. Ene adducts of **1** were obtained with alkenes **7a-e**, not, however, with allylbenzene. The *cis*-fixed 1,3-diene **10** and **1** gave rise to a 48% yield of **11**, whereas **10** and **4**, the higher homologue of **1**, led to a 27% yield of **14**.

Some time ago, we were able to generate tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene (**1**) by treatment of 1-chlorotricyclo[3.1.0.0^{2,6}]hexane (**2b**) with strong bases. This short-lived intermediate could be trapped as a Diels-Alder adduct with some cyclic 1,3-dienes such as anthracene, 2,5-dimethylfuran, diphenylisobenzofuran [1] and 1,2,3-trimethylisoindole,[2] whereas good nucleophiles lead to 1-substituted tricyclo[3.1.0.0^{2,6}]hexane derivatives. In addition to the dehydrohalogenation of **2b** the bridgehead olefin **1** could also be generated from the silane **2c** with cesium fluoride in dimethyl sulfoxide.[1] In some aspects the behaviour of **1** is reminiscent of the chemistry of benzyne **3**.[3] This led us to search for ene reactions of **1** which have so far not been observed for bicyclo[1.1.0]but-1(3)-ene derivatives. Here we report on a modified generation of **1**, on some ene reactions [4] of **1** and on results of attempts to trap **1** and its higher homologue **4** in some Diels-Alder reactions.


1



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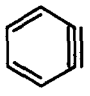
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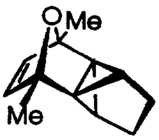


5

2	a	b	c	d	e	f	g	h	i
R^1	H	Cl	Br	Li	Br	Br	Br	Br	Li
R^2	H	H	SiMe$_3$	Li	Br	Li	D	H	H

A. *1,6-Dibromtricyclo[3.1.0.0^{2,6}]hexane as a Source for Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene*

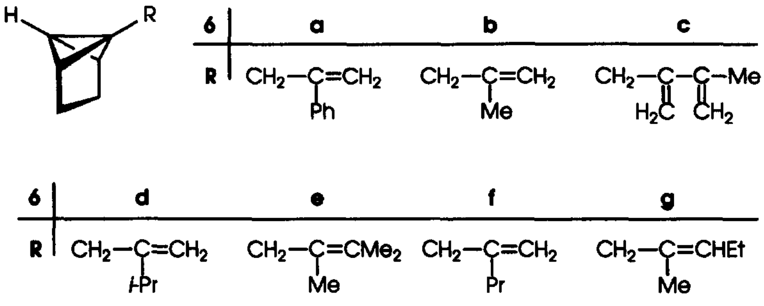
Tricyclo[3.1.0.0^{2,6}]hexane **2a** has been shown to be one of the few bicyclo[1.1.0]butanes that can be metalated with 2.0 equiv. of *n*-butyllithium (BuLi) in ether at both bridgehead positions to give **2d** in high yield.[5] The reaction of **2d** with 2.5 equiv. of 4-tolylsulfonyl bromide (TsBr) at 0°C in ether afforded a 56%

yield of the dibromide **2e**. The sequential bromination of **2d** leaves no doubt that **2f** is formed as an intermediate in this reaction. Therefore, it is safe to assume that under appropriate reaction conditions (at 0°C or below) **2f** does not eliminate lithium bromide spontaneously forming the bridge-head olefin **1**. The assumption that **2f** is reasonably stable at -78°C could easily be proved experimentally. After the reaction of the dibromide **2e** with 2.0 equiv. of *tert*-butyllithium (*t*-BuLi) in THF/pentane at -78°C and addition of [OD]methanol afforded a 36% yield of 1-bromo-[6-D]tricyclo[3.1.0.0^{2,6}]hexane **2g**.

The dibromide **2e** was found to be a valuable starting material for generating **1**. When treated with magnesium, lithium sand or with *t*-BuLi (2.0 equiv.) in the presence of 2,5-dimethylfuran the known propellane **5**[1] was isolated in yields of 43, 57 and 40%. These results indicate that tricyclohexene **1** can be produced under a wider range of reaction conditions than was possible previously.

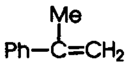
B. Some Ene Reactions of Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene

Best results of the ene reactions of **1** were obtained, when the dibromide **2e** was converted into **2f** with 2 equiv. of *t*-BuLi at -78°C and the cooled solution was transferred by cannula technique to a solution of the ene component in THF. In the presence of α-methylstyrene (**7a**) **6a** was isolated in 78% yield. **1** and isobutene (**7b**) led to **6b** in a modest yield of only 15%, while 2,3-dimethyl-1,3-butadiene (**7c**) afforded a 37% yield of the diene **6c**. Side-products of unknown structure prevented the purification of **6c**. From the NMR spectroscopic data, the structure of **6c** could be established beyond doubt; at the same time, the spectra did not show any indications for the formation of the Diels-Alder adduct **8**.



6	**a**	**b**	**c**
R	$CH_2-C(Ph)=CH_2$	$CH_2-C(Me)=CH_2$	$CH_2-C(=CH_2)-C(=CH_2)-Me$

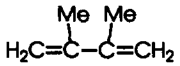
6	**d**	**e**	**f**	**g**
R	$CH_2-C(i\text{-}Pr)=CH_2$	$CH_2-C(Me)=CMe_2$	$CH_2-C(Pr)=CH_2$	$CH_2-C(Me)=CHEt$


$Ph-C(Me)=CH_2$

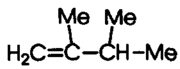
7a

$Me_2C=CH_2$

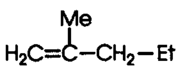
7b


$H_2C=C(Me)-C(Me)=CH_2$

7c


$H_2C=C(Me)-CH(Me)-Me$

7d


$H_2C=C(Me)-CH_2-Et$

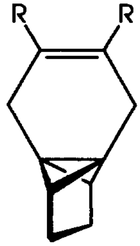
7e

$Ph-CH_2-CH=CH_2$

7f

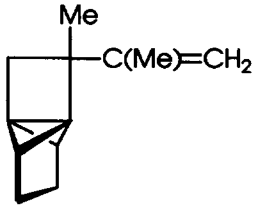
In addition to the methyl hydrogen atoms, alkenes **7d** and **e** hold also methyne or methylene protons in allylic positions. Therefore, the ene reaction of **1** with **7d** could lead to **6d** and **e**, and with **7e** to **6f** and **g**. The NMR analysis of the ene reaction of **1** with **7d** showed that only **6d** was formed in 20% yield. In contrast, the generation of **1** in the presence of **7e** afforded, according to NMR analysis, a 7·3 mixture of **6f** and **6g** in a total yield of 18%. From the ^{13}C NMR spectrum it could be deduced that **6g** was formed as a 2:1 *cis-trans* mixture The compounds could not be separated. Steric factors seem to play an important role in the ene reaction The preference of the shift of a methyl proton as compared to methylene or methine hydrogens was observed in the competitive ene reaction of diethyl azodicarboxylate with appropriate alkenes[6] In the intramolecular competition of diethyl azodicarboxylate with 2-methyl-1-butene the methylene hydrogen migrated slightly faster than the methyl hydrogens.[6]

Besides ene and Diels-Alder adducts, the reaction of dehydrobenzene **3** with 2,3-dimethylbutadiene **7c** produced also a [2+2] cyclo-adduct.[7] The analogue reaction of **1** with **7c** would lead to the [2 1 1]propellane **9**. To the best of our knowledge it is safe to assume that **9** is not stable at room temperature[8,9] In accord with this prediction, no indication for the formation of **9** could be obtained



a: R = Me
b: R = H

8



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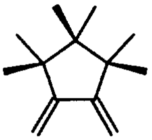
C. Diels-Alder Reactions of Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene

Diels-Alder trapping reactions of the bicyclo[1 1 0]but-1(3)-ene derivates **1**, **4** and further 2,4-bridged bicyclobutenes were successful only with *endo*-cyclic, *cis*-fixed 1,3-dienes, like anthracene, furans, diphenyl-



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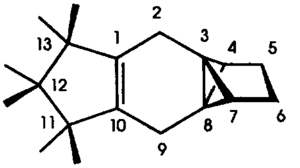

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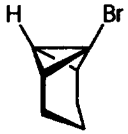

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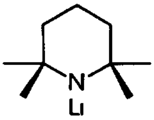

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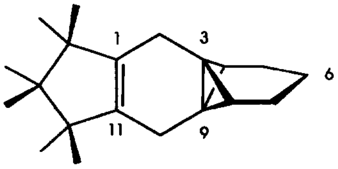

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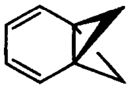

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isobenzofuran and isoindoles[10] The reaction of dibromide **2e** with *t*-BuLi at -78°C to give **2f** and attempts of generating **1** and trapping it with 1,3-butadiene did not afford the desired cyclo-adduct **8b** However, the *cis*-

fixed 1,3-diene system in **10** met the precondition for a successful Diels-Alder reaction with **1** Adduct **11** was isolated in 48% yield Carrying out the same reaction with **4**, generated from bromide **12** and lithium 2,2,6,6-tetramethylpiperidide **13**, propellane **14** was formed in 27% yield

After we had prepared the propellanes **11** and **15** the next obvious step was to try to convert these compounds to the corresponding [4 1.1]propelladienes of substructure **15** by addition of bromine and elimination of two molecules of hydrogen bromide Unfortunately, the addition of bromine to **11** led only to a complex mixture of products, in which the bicyclo[1 1 0]butane ring was completely destroyed

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EXPERIMENTAL

I. General Remarks

Solvents were purified by standard procedures Tetrahydrofuran (THF) was freshly distilled from potassium metal. All air-sensitive reactions were carried out under nitrogen in flame-dried glassware

Tricyclo[3 1 0 0^{2,6}]hexane (**2a**),[11] 1-bromotricyclo[3 1 0 0^{2,6}]hexane (**2h**),[12] (6-bromotricyclo[3 1 0 0^{2,6}]hex-1-yl)-trimethylsilane (**2c**),[1] 1-bromotricylo[4 1 0 0^{2,7}]heptane (**12**),[13] 4-tolylsulfonyl bromide (TsBr),[14] lithium 2,2,6,6-tetramethylpiperidide (**13**),[15] and 1,1,2,2,3,3-hexamethyl-4,5-bis(methylene)cyclopentane (**10**)[16] were prepared by reported procedures *tert*-Butyllithium (*t*-BuLi) in pentane was obtained from ALDRICH, *n*-butyllithium (BuLi) in hexane from CHEMETALL, the content of these solutions was determined prior to use by standard methods [17, 18]

II. 1,6-Dibromotricyclo[3.1.0.0^{2,6}]hexane (2e), Generation of 1-Bromotricyclo[3.1.0 0^{2,6}]hex-6-yllithium (2f) and Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene (1) from 2e

1 Synthesis of **2e**: **2a** (10.0 g, 125 mmol) was added dropwise at 0°C to a solution of BuLi (312 mmol) in ether (200 ml) and the mixture stirred for 7 d at room temperature (rt) The suspension containing tricyclo[3 1 0 0$^{2 6}$]hex-1,6-diyldilithium (**2d**) was transferred into a dropping funnel and added to a solution of TsBr (73 5 g, 313 mmol) in ether (250 ml) at 0°C under vigorous stirring Stirring was continued for 2 h, the mixture hydrolysed with a 2 N solution of ammonia (100 ml) and extracted with water (500 ml) Distillative workup of the organic layer using a 20 cm Vigreux column afforded **2e** (16 54 g, 56%), b p 66-67°C/12 mmHg ^{1}H NMR ($CDCl_3$) δ 1 53 (s, 4 H, 3-, 4-H_2), 2 52 (s, 2 H, 2-, 5-H) ^{13}C NMR ($CDCl_3$) δ 24 50 (s, C-1, -6), 25 99 (t, C-3, -4), 48 58 (d, C-2, -5), MS (70 eV) m/z (%) 240 (25), 238 (50) [M^+], 236 (25), 159 (33), 157 (33), 78 (100), 77 (100), 51 (50), 50 (30), 41 (5), 39 (8), 38 (10), M^+ calc 235 884, obsd 235 885

2 Generation of **2f** *t*-BuLi (8 40 mmol) in pentane was added to a solution of **2e** (1 00 g, 4 20 mmol) in THF (10 ml) at -78°C under nitrogen atmosphere The yellow solution was stirred for 1 h at -78°C, then methan[D]ol (300 µl, 7 39 mmol) was injected by syringe and the mixture was warmed up to rt Distillative workup afforded 1-bromo-[6-D]tricyclo[3 1 0 0$^{2 6}$]hexane (**2g**) (240 mg, 36%) containing traces of THF, b. p. 30°C/0.1 mmHg ^{1}H NMR ($CDCl_3$) δ 1.39 (m, 4 H, 3-, 4-H_2), 2 35 (s, 2 H, 2-, 5-H) The 6-H signal of bromotricyclo[3.1 0.0^{2,6}]hexane (**2h**) [12] at δ 2 34 is missing in the spectrum of **2g**

*3. Generation of Tricyclo[3 1.0.0 ^{2,6}]hex-1(6)-ene (1) from **2e** in the Presence of 2,5-Dimethylfuran*

*a **2e** with magnesium in THF*: **2e** (700 mg, 2 94 mmol) in THF (5 ml) was added to a mixture of magnesium turnings (400 mg, 16.5 mmol) and 2,5-dimethylfuran (1 00 ml, 9 39 mmol) in THF (5 ml). After stirring for 4 h under reflux and another 12 h at rt the solvent was removed in vacuo and the unvolatile material was treated with ether and water The ether solution was dried over $MgSO_4$, the solvent removed under vacuum and the remaing oil analyzed by NMR spectroscopy, indicating the formation of 1,8-dimethyl-11-oxapentacyclo[6.2 1.$0^{2,6}$.$0^{2,7}$.$0^{3,9}$]undec-9-ene (**5**)[1] (43%) accompanied by traces of unreacted 2,5-dimethylfuran

*b **2e** with lithium sand in ether*: A solution of **2e** (700 mg, 2 94 mmol) in ether (5 ml) was slowly added to a mixture of lithium sand[19] (1 50 g, 216 mmol) and 2,5-dimethylfuran (680 µl, 6 39 mmol) in ether (10 ml) The first drops of the solution of **2e** caused a vigorous reaction. The addition of **2e** was carried out at a rate that kept the mixture constantly under reflux. After stirring for 1 h at rt the solution was separated from solid residues by filtration. Water was added, the ether layer separated and the solvent removed under reduced pressure ^{1}H NMR analyses of the residual oil showed the presence of Diels-Alder adduct **5** (57%) and 2,5-dimethylfuran

*c **2e** with t-BuLi in THF*: *t*-BuLi (8 40 mmol) in pentane was added to a solution of **2e** (1 00 g, 4 20 mmol) in THF (10 ml) at -78°C and stirred for 1 h at this temp The mixture was pumped by N_2 pressure via a cannula (Ø ca 2 mm) into a flask containing 2,5-dimethylfuran (890 µl, 8 36 mmol) in THF (10 ml) The solution was stirred for 1 h and the solvent was removed under reduced pressure The residue was distilled at 60°C (bath) and 10^{3} mmHg ^{1}H NMR analysis showed that **5** had been formed in 40% yield.

III. Ene Reactions of 1

1 With 2-phenylpropene (7a) A solution of **2f** was prepared from **2e** (1 50 g, 6 30 mmol) in THF (10 ml) and *t*-BuLi (12 6 mmol) in pentane by following the procedure II 3.c This solution was transferred via cannula into a mixture of **7a** (3 00 g, 25 4 mmol) in THF (10 ml). After stirring the solution for 2 h and removal of the solvent under reduced pressure, the residue was dissolved in ether (15 ml) and the solution extracted with a 2 N solution of aqueous ammonia (10 ml) Distillation of the residue of the organic layer afforded 1-(2-phenyl-3-propenyl)tricyclo[3 1 0 $0^{2,6}$]hexane (**6a**) (970 mg, 78%) as a colourless liquid, b p 36-40°C (bath)/0 001 mmHg IR (film) 3082 cm^{1}, 3032, 2946, 2868, 1629, 1601, 1575, 1495, 1029, 982, 898, 779, 700 ^{1}H NMR (CDCl$_3$) δ 1 22 (s, 4 H, 3-, 4-H$_2$), 1 56 (s, 1 H, 6-H), 1 88 (s, 2 H, 2-, 5-H), 3 09 (s, 2 H, *C*H$_2$-C(Ph)=CH$_2$), 5 09 and 5 31 (2s, 1 H, vinyl H), 7.30 (m, 5 H, aromatic H) ^{13}C NMR (CDCl$_3$) δ 7.11 (d, C-6), 15.40 (s, C-1), 26 29 (m, C-3, -4), 32 03 (t, *C*H$_2$-C(Ph)=CH$_2$), 36 76 (d, C-2, -5), 112 53 (t, =CH$_2$), 126 06, 128.13 (2 d, 2*2 aromatic C), 127.28 (d, aromatic C), 141.38 (s, aromatic C), 147 73 (s, *C*(Ph)=CH$_2$). MS (70 eV) m/z (%) 196 (20) [M$^+$], 195 (26), 168 (100), 167 (72), 166 (23), 165 (34), 155 (25), 117 (24), 115 (39), 103 (46), 91 (51), 79 (32), 78 (23), 77 (59)

2 With 2-methylpropene (7b) **7b** (80 ml) was condensed in a three-necked flask, which was cooled to -78°C and equipped with a dry-ice condenser. Then a solution of **2f** (6 30 mmol, prepared from **2e** according to II 3.c) was added through a cannula The mixture was kept under reflux for 30 min. The solvent and unreacted **7b** were removed by distillation at rt under reduced pressure Aqueous workup and distillation of the organic layer afforded 1-(2-methyl-3-propenyl)tricyclo[3 1.0 $0^{2,6}$]hexane (**6b**) (130 mg, 15%) as a colourless liquid, b p 0°C (bath)/0 001 mmHg ^{1}H NMR ($CDCl_3$). δ 1 28 (s, broad, 4 H, 3-, 4-H_2), 1 61 (m, 1 H, 6-H), 1 71 (s, 3 H, CH_3), 1 90 (s, broad, 2 H, 2-, 5-H), 2 62 (s, 2 H, CH_2-C(CMe=CH_2), 4 70 (narrow m, 2 H, =CH_2) ^{13}C NMR ($CDCl_3$)· δ 6 85 (d, C-6), 15 18 (s, C-1), 22 54 (q, CH_3), 26.35 (m, C-3, -4), 34.53 (t, CH_2-C(Me)=CH_2), 36.62 (d, C-2, -5), 110 16 (t, =CH_2), 149 42 (s, *C*(Me)=CH_2) (Found C, 89 02; H, 10 44 Calc for $C_{10}H_{14}$ C, 89.49, H, 10 51)

3 With 2,3-dimethyl-1,3-butadiene (7c) A solution of **2f**, obtained by reacting **2e** (1 08 g, 4 54 mmol) and *t*-BuLi (9 10 mmol) in pentane in accordance to II 3 c, was transferred via cannula into a solution of **7c** (7 63 mg, 9 29 mmol) in THF (10 ml) The orange-coloured solution was stirred for 1 h at rt, the solvent was removed under reduced pressure and the residual oil treated with ether (10 ml) and 2 N aqueous ammonia Distillative workup of the organic layer afforded a colourless liquid (443 mg), b p 60-61°C(bath)/10^{-3} mmHg ^{1}H NMR analysis of the material showed the formation of a mixture of 2-(1-tricyclo[3 1 0 0^{2,6}]hexylmethyl)-3-methyl-1,3-butadiene (**6c**, yield 37%) as the major component and material of unknown constitution Spectroscopic data of **6c** ^{1}H NMR ($CDCl_3$) δ 1 28 (m, 4 H, 3-, 4-H_2), 1 63 (s, 1 H, 6-H), 1 88 (s, 3 H, CH_3), 2 35 (m, 2 H, 2-, 5-H), 2 85 (s, 2 H, CH_2), 5 00 (m, 4 H, vinylic H) ^{13}C NMR ($CDCl_3$) δ 7 66 (d, C-6), 15 90 (s, C-1), 21 57 (q, CH_3), 26 87 (m, C-3, -4), 30 90 (t, CH_2), 37 44 (d, C-2, -5), 113 10 (t, 2 C, =CH_2), 143 33 and 147 69 (s, vinylic C)

4 With 2,3-dimethyl-1-butene (7d) A solution of **2f**, obtained by following the procedure II 3.c by reaction of **2e** (1.41 g, 5.93 mmol) and *t*-BuLi (11 9 mmol) at -78°C, was transferred via cannula into a solution of **7d** (2 50 g, 29 7 mmol) in THF (15 ml) The mixture was stirred for 1 h at rt, the solvent was removed under reduced pressure, and the residual oil treated with ether (10 ml) and a 2 N solution of aqueous ammonia Distillative workup of the organic layer afforded 2-(1-tricyclo[3 1 0 0^{2,6}]hexylmethyl)-3-methyl-1-butene (**6d**) (201 mg, 21%) as a colourless liquid, b p 24°C (bath)/10^{3} mmHg IR (film) 3034 cm^{-1}, 2952, 2870, 1724, 1449, 1178 ^{1}H-NMR ($CDCl_3$) δ 1 00 (d, J=7 5 Hz, 6 H, Me), 1 30 (m, 4 H, 3-, 4-H_2), 1 65 (s, 1 H, 6-H), 1 93 (m, 2 H, 2-, 5-H), 2 21 (sept, J=7 5 Hz, 1 H, *H*-CMe_2), 2 63 (s, 2 H, CH_2-C=CH_2), 4 71 (sd, 2 H, =CH_2) ^{13}C-NMR ($CDCl_3$)· δ 6 85 (d, C-6), 15 24 (s, C-1), 21 78 (q, Me), 26 41 (m, C-3, -4), 31 62 (t, H_2C-C=CH_2), 36 80 (d, C-2,-5), 38 61 (d, $HCMe_2$), 107 04 (t, =CH_2), 155 62 (s, *C*=CH_2) MS (70 eV)· m/z (%) 162 (1) [M^+], 147 (24), 119 (72), 105 (25), 91 (100), 79 (66), 77 (38), 57 (23), 41 (44) (Found C, 89 23; H, 11 21 Calc for $C_{12}H_{18}$ C, 88 82, H, 11 18)

5 With 2-methyl-1-pentene (7e) A solution of **2f**, obtained according to II 3 c by reaction of **2e** (1 50 g, 6 30 mmol) and *t*-BuLi (12 6 mmol) was added via cannula to a solution of **7e** (530 mg, 6.30 mmol) in THF (10 ml) and stirred for 2 h at rt After removal of the solvent in vacuo and aqueous workup, distillation of the crude product afforded 170 mg (17%) of an ene adduct mixture as a colourless liquid, b p 25°C (bath)/10^{-3} mmHg According to NMR analysis, the product consists of a 70 30 mixture of 2-(1-tricyclo[3 1 0 0$^{2\,6}$]hexylmethyl)-1-pentene (**6f**) and 2-(1-tricyclo[3 1 0 0^{2,6}]hexylmethyl)-2-pentene (**6g**, as a 2 1 *cis-trans* mixture) Data of **6f** IR (film) 3033 cm^{1}, 2948, 2870, 1728, 1647, 1455, 1177, 889 ^{1}H NMR ($CDCl_3$) δ 0 88 (t, J=7 5 Hz, 3 H, CH_3), 1 28 (broad s, 4 H, 3-, 4-H_2), 1 57 (m, 3 H, 6-H, CH_2Me), 1 89 (broad s, 2 H, 2-, 5-H), 1 96 (m, 2 H, =CH-CH_2-CH_2), 2 58 (s, 2 H, -CH_2-C=), 4 75 (broad s, 2 H, =CH_2) ^{13}C NMR ($CDCl_3$) δ 6 85 (d, C-6), 13 87 (q, Me), 15 14 (s, C-1), 20 82 (t, Me-CH_2), 26 38 (m, C-3, -4), 32 95 (t, =C-CH_2-CH_2), 36 68 (d, C-2, -5), 39 29 (t, CH_2-C=), 109 25 (t, =CH_2), 149 42 (s, =C) MS (70 eV) m/z (%) 162 (13) [M^+], 147 (17), 133 (38), 119 (78), 105 (45), 91 (100), 79 (58), 77 (37), 57(30)

In addition, the ^{1}H NMR spectrum of the product mixture showed signals at δ 4 50-4 78 (narrow m) and δ 4 97-5 28 In the ^{13}C NMR spectrum there were olefinic signals at δ 127 12 (d) and 133 70 (s) for the major component (*cis* **6g**) and at δ 126 61 (d) and 145 50 (s) for the minor component (*trans* **6g**)
(Found· C, 88 52, H, 10 94 Calc for $C_{12}H_{18}$ C, 88 82, H, 11 18)

6 With allylbenzene (7f) A solution of **2f**, prepared according to II 3 c from **2e** (1 00 g, 4 20 mmol) and *t*-BuLi (8 40 mmol), was transferred via cannula into a solution of allylbenzene (1 98 g, 16 8 mmol) in THF (10 ml) The mixture was stirred for 2 h at rt The usual workup afforded a residual oil, the NMR spectra of which did not show any indications of the formation of an ene adduct

IV. Some Diels-Alder Reactions of Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene (1) and Tricyclo[4.1.0 0^{2,7}]hept-1(7)-ene (4)

1 1 and 1,3-butadiene A solution of **2f** was prepared by reaction of **2e** (1 00 g, 4 20 mmol) in ether (10 ml) and *t*-BuLi (8 40 mmol) at -78°C The solvent was removed under reduced pressure (10^{-3} mmHg) within 1 5 h at -78°C 1,3-Butadiene (50 ml) was condensed into the reaction vessel containing **2f** as a colourless powder, and, under evaporation of 1,3-butadiene, the suspension was slowly warmed up to rt Distillation of the residual oil afforded a small amount of a liquid, the spectra of which did not show any indications of the formation of a Diels-Alder adduct

2 1 and 1,1,2,2,3,3-hexamethyl-4,5-bis(methylene)cyclopentane (10) A solution of **2h** (1 05 g, 6 60 mmol) in THF (10 ml) was slowly added during 1 5 h at -30 to -35°C to a solution of **13** (9 85 mmol) and **10** (1 30 g, 7 29 mmol) in THF (10 ml) The mixture was stirred for 36 h at -30°C, warmed to rt, and the solvent was removed under reduced pressure Addition of ether (10 ml), water (10 ml) and 2 N aqueous ammonia (3 ml) followed by distillative workup of the organic layer afforded 11,11,12,12,13,13-hexamethylpentacyclo-[8 3 0 $0^{3,7}$ $0^{3,8}$ $0^{4,8}$]tridec-1(10)-ene (**11**) (818 mg, 48%) as a colourless liquid, b p 70-72°C/10^{3} mmHg which crystallized at -30°C to give colourless needles of m p of 28-29°C IR (film) 3029 cm^{1}, 2924, 2828, 1650, 1478, 1458, 1442, 1393, 1374, 1125, 596 ^{1}H NMR ($CDCl_3$) δ 0 78 (s, 6 H, CH_3), 0 87 (s, 12 H, CH_3), 1 33 (s, 4 H, 5-, 6-H_2), 2 03 (s, 2 H, 4-, 7 -H), 2 38 (s, 4 H, 2-, 9-H_2) ^{13}C NMR ($CDCl_3$)· δ 11 21 (s, C-3, -8), 17 78 (t, C-2, -9), 21 48 (q, 2 C, CH_3), 23 90 (q, 4 C, CH_3), 27 14 (t, C-5, -6), 44 71 (d, C-4, -7), 48 01 (s, C-11, -13), 48 22 (s, C-12), 136 16 (s, C-1, -10) MS (70 eV) m/z (%) 256 (53) [M^+], 241 (100), 172 (50), 129 (28), 126 (31), 91 (34), 69 (37), 55 (34), 41 (69), M^+ calc 256 219, obsd 256 219 (Found C, 87 51, H, 10 68 Calc for $C_{19}H_{28}$ C, 88 99, H, 11 01)

3 4 and 10 To a solution of amide **13** (6 66 mmol) and diene **10** (790 mg, 4 43 mmol) in THF (10 ml) was added a solution of **12** (770 mg, 4 45 mmol) during 1 5 h at -35°C The mixture was kept at -30°C for 24 h After warming up to rt, the solvent was removed in vacuo and the residual oil was treated with ether (10 ml), water (10 ml) and a 2 N solution of aqueous ammonia (3 ml) Distillative workup of the organic layer afforded 12,12,13,13,14,14-hexamethylpentacyclo[9 3 0 $0^{3,8}$ $0^{3 9}$ $0^{4 9}$]tetradec-1(10)-ene (**14**) (326 mg, 27%) as a colourless liquid, b p 65-67°C/10^{3} mmHg that, on cooling, afforded colourless needles of m p 30-31°C IR (film) 2934 cm^{1}, 2817, 1476, 1454, 1442, 1378, 1150, 977 ^{1}H-NMR ($CDCl_3$) δ 0 76 (s, 6 H, CH_3), 0 83 (s, 12 H, CH_3), 1 34 (broad s, 6 H, 5-, 6-, 7-H_2), 2 33 (broad s, 6 H, 2-, 10-H_2, 4-, 8-H) ^{13}C NMR ($CDCl_3$) δ 13 99 (s, C-3, -9), 20 54 (t, C-5, -7), 20 99 (t, C-6), 21 41 (t, C-2, -10), 21.51 (q, 2 C, CH_3), 23 87 (q, 4 C, CH_3), 47 98 (s, C-13), 48 07 (s, C-12, -14), 134 45 (s, C-1, -11) MS (70 eV) m/z (%) 270 (72) [M^+], 255

(100), 240 (8), 225 (10), 220 (10), 213 (14), 199 (14), 186 (76), 171 (64), 159 (32), 143 (42), 105 (32), 91 (52), 77 (36), 69 (48), 55 (52).

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