# EN ROUTE TO TETRA-t-BUTYLETHYLENE†

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Abstract—Triene 22 was synthesized and converted by two different routes to the tetraaldehyde 27, the first "non-bridged" derivative of 1. An X-ray analysis of 27 reveals that the C=C bond is twisted by 28.6°. Attempts to prepare 1 from 27 failed, thus far. Addition of t-butyllithium to 13, subsequent reaction with ethylene oxide and further reactions led to the highly strained tri-t-butylethylethylethylethylene 33; according to force field calculations 33 has the largest fragmentation strain of all synthesized hydrocarbons of this type.

Deviations of structural parameters from the normal values are of considerable interest to chemists because they contribute significantly to the understanding of chemical bonding and reactivity. These deviations may be caused by ring strain or by the repulsive interactions of bulky substituents. In the case of sterically hindered alkenes they can lead to stretching, torsion and out-ofplane deformation of the C=C bond; in addition stretching of the adjacent C-C bonds and angle deformations in other parts of the molecule can occur. All these deformations can lead to a change in spectroscopic properties and reactivity.

Crowding in organic compounds can be induced by many different combinations of groups, but the t-Bu substituent is the most used because its size and symmetry simplifies the interactions and the spectra. For this reason, tetra-t-butylethylene (1) has been the synthetic goal of many research groups for the last ten years.<sup>1-12</sup>

# Previous synthetic approaches to 1

Synthesis of crowded structures has been a demanding task, since the large groups often preclude the use of methods that are successful for less-strained analogues, and the sterically crowded branched structures themselves are often prone to rearrangements which lead to less-strained structures. Two basically different concepts have been used in the synthesis of 1.

(1) Combination of two synthons each of which contains two t-Bu groups; the C=C bond is formed in the last step of the synthesis.

(2) Generation of the C=C bond in an early step of the synthesis; the t-Bu groups are then formed in the last step of the synthesis.

Attempts to couple two molecules of dibutylketone (2) with low-valent titanium compounds (McMurry method),<sup>9</sup> of di-t-butyldihalomethane (3) with metals<sup>10,11</sup> or of di-t-butyldiazomethane (4) by photolytic decomposition<sup>12</sup> did not yield 1 (Concept 1). In addition, it was not possible to prepare 1 by a combination of 4 and the corresponding thione or selone 5 and subsequent loss of nitrogen and sulfur or selenium.<sup>1,2</sup> Since all these methods, particularly the



McMurry reaction and the thia- or selenadiazoline method were used successfully in the syntheses of varions, although less-hindered alkenes, this failure is apparently due to the intramolecular steric repulsion of the four t-Bu groups.

To decrease this detrimental interaction "tied back" intermediates were used in order to form the t-Bu groups after generation of the C==C bond (Concept 2).



Boerma was the first who applied this general approach to the synthesis of  $1.^{13}$  He prepared the diazo compound 6; however, attempts at the dimerization of the corresponding carbene failed.<sup>13</sup> Later thione 7a<sup>7</sup> and selone 7b<sup>14</sup> were prepared, but it was not possible to obtain alkenes 8 and 9 via the thia-<sup>7,17</sup> or



selenadiazoline route,<sup>14</sup> since steric hindrance could still not be overcome. However, alkene 10 was prepared via the thiadiazoline method in good yield;<sup>7,15</sup> therefore, the less strained 22, which could serve as a precursor for the synthesis of 1, should also be accessible.

Precursors 8-10 and 22 are "geminally" bridged compounds; however, for the synthesis of 1 "vicinally"

<sup>†</sup> Sterically hindered alkenes, Part 8. For Part 7 see Ref. 36.



bridged precursors, such as 11 or 12, can also be envisaged. For this reason, we attempted the synthesis of 11 and related compounds via addition reactions to the angle strained cycloalkyne 13.

### Synthesis of 22

From the diketone 14<sup>18,19</sup> the unsaturated ketone 16



was prepared via selective reduction of one carbonyl group and a subsequent elimination reaction from the ketoalcohol 15. Hydrazone 17 served as the starting material for the diazo compound 18 as well as for the thioketone 19. 1,3-Dipolar cycloaddition of 18 and 19 led to the thiadiazoline 20 which on thermal decomposition yielded the alkene 22 via the thiirane 21.

Alkene 22, which was synthesized independently by Guziec and coworkers<sup>20</sup> via the corresponding selenadiazoline, exhibits two bands in the Raman spectrum for the central C=C bond stretching at 1563 and 1536 cm<sup>-1</sup>, respectively; this is evidence for considerable strain in the region of the C=C bond.<sup>21</sup>

# Attempts at the synthesis of 1 from 22

Starting from 22 it is necessary to cleave the two double bonds in the 5-membered rings without affecting the central double bond, which is much more shielded. The two classical methods for the cleavage of double bonds, ozonization and hydroxylation with subsequent oxidative cleavage with sodium periodate were applied.



Hydroxylation of 22 with  $OsO_4$  led after cleavage of the cyclic osmium esters to tetraol 23 and diol 24. Good yields (up to 71%) of 23 were only obtained using 2 mol of  $OsO_4$ , whereas the catalytic oxidation using potassium chlorate as oxidant gave only poor yields of 23. Two syn-anti stereoisomers, 23a and b were observed in the <sup>1</sup>H-NMR spectrum, but were not separated since both can be used in the subsequent glycol cleavage. Preparation of tetraol 23 from 24 with  $OsO_4$  was only possible after protection of the hydroxy groups with methoxypropene. Compound 25 was



hydroxylated with  $OsO_4$  in excellent yield to give 26, which on hydrolysis yielded the expected 23. Reaction of 23 with periodate gave two products, the tetraaldehyde 27 (26%) and the dialdehyde 28. The



enedial 24 was also converted to the corresponding enedialdehyde by treatment with periodate.

Thus, the synthesis of the desired tetraaldehyde, the first unbridged derivative of tetra-t-butylethylene (1), was achieved, but the yields, particularly in the last step, and the duration of the hydroxylation (several weeks) were unsatisfactory.

Therefore, ozonization of 22 was attempted. However, only with ethylacetate as solvent and TCNE as reducing agent could a good (50–60%) yield of 27 be obtained.

The tetraaldehyde 27 is a colorless solid, which melts at 140° with decomposition. The EI mass spectrum does not show the molecular ion peak, but the CI mass spectrum (isobutane) gives the molecular ion at m/e 309 as the most intense peak. The <sup>1</sup>H-NMR spectrum exhibits at 35° only two singlets at  $\delta$  1.43 (CH<sub>3</sub>) and 9.41 (CHO) ppm; at  $-43^{\circ}$  two peaks of equal intensity are observed for the CH<sub>3</sub> groups. From the coalescence temperature  $T_c = -26^\circ$  (400 MHz,  $CD_2Cl_2$ -CFCl<sub>3</sub> 1:3), and the shift difference,  $\Delta v = 33.4$  Hz, a free enthalpy of activation  $\Delta G^{\ddagger} = 12.2 \text{ kcal mol}^{-1}$ , for the rotation about the allylic bonds can be estimated. At lower temperatures further changes occur in the <sup>1</sup>H-NMR spectrum. The IR spectrum of 27 shows the C=O stretching vibration at 1730 cm<sup>-1</sup>, the C=C stretching mode cannot be observed. However, the Raman spectrum shows a strong band at 1461  $cm^{-1}$  in which the C=C stretching vibration and the CH<sub>2</sub> deformations overlap. This is the lowest value for a C==C stretching vibration.

The UV spectrum shows two bands at  $\lambda(z)$  207 (2150) and 241 (1500) nm in cyclohexane. The first band is assigned to the  $n \rightarrow \sigma^*$  transition of the C=O groups, the second band to the  $\pi \rightarrow \pi^*$  transition of the C=C bond. The shift of the  $\pi \rightarrow \pi^*$  band from about 180 nm in a normal tetraalkyl-substituted ethylene to 241 nm indicates a considerable change in the electron distribution of this C=C bond compared to "normal" alkenes. This is in accord with a significant bond length

Raman vc-c(cm <sup>-1</sup> )	UV λ (s) (nm)	<sup>13</sup> C-NMR C==C (p <b>fin</b> )	Ref.
1604	204.0 (7000)	143.60	22
1560	217.0 (13,800)	142.32	25
1470	,		-
1540	203.0 (15,100)	149.78	7
1563	219.6 (3300)	151.27	24
1536	( )		
1490	228.0 (4890)	150.56	21
	· · ·	151.17	
1516	234.0 (5000)	145.10	11
	· · · · ·	152.60	
1461	207.0 (2150)	150.17	11
	241.0 (1500)		
~1475	245.0 (3700)	152.35	25
		154.45	
	Raman v <sub>c~c</sub> (cm <sup>-1</sup> ) 1686 1580 1470 1540 1563 1536 1490 1516 1461 ~1475	Raman         UV $\nu_{c-c}(cm^{-1})$ $\lambda$ (a) (nm)           1698         204.0 (7000)           1580         217.0 (13,800)           1470         203.0 (15,100)           1540         203.0 (15,100)           1563         219.6 (3300)           1536         228.0 (4890)           1516         234.0 (5000)           1461         207.0 (2150)           241.0 (1500)         ~1475	Raman $v_{c-c}(cm^{-1})$ UV $\lambda$ (a) (nm) ${}^{13}C-NMR$ C=C (pfm)1698 1580 1580 1580 1540 1563 1563 1630203.0 (17.000) 143.600 142.32143.60 142.321470 1540 1563 

Table 1. Some spectroscopic data of sterically hindered alkenes

Table 2. Some C—C bond lengths (pm), C—C—C bond angles (°) and C—C—C—C dibedral angles (°) of 27

C1-C2	135.7 (13)	C3-C1-C4	112.5 (7)
C1-C3	159.7 (11)	C2-C1-C4	123.8 (8)
C1C4	157.3 (11)	C2-C1-C3	123.6 (7)
C2C5	156.7 (11)	C1-C2-C6	123.9 (7)
C2C6	155.5 (10)	C1-C2-C5	121.9 (7)
C3C9	158.3 (11)	C5-C2-C6	114.2 (7)
C4-C12	156.9 (13)	C8-C3-C9	96.6 (6)
C5-C15	155.6 (10)	C10-C4-C12	95.9 (6)
C6-C18	153.8 (12)	C14C5C15	94.9 (6)
		C16-C6-C18	95.6 (6)
	C3C1C2C5	28.6 (1.2)	
	C4C1C2C6	28.6 (1.2)	

Table 3. Dihedral angles and C=C bond lengths of some twisted, sterically crowded alkenes

	Dihedral angle (°)	C=C bond length (pm)	Rcí.
27	28.6	135.7	This work
30	19.7	135.3	8
34	21.8	135.8	27
	7.3		
35	16.0	135.3	28
36	12.3	135.8	29
37	11.8	134.9	30

change and a large twist of the C=C bond. Table 1 presents some spectroscopic data of highly hindered olefins. Single crystals of 27 were obtained from acetonitrile. Table 2 shows some results of the X-ray analysis.<sup>36</sup>



† Average value of a search in the Cambridge File between 1972 and 1982 from 40 publications.

The largest deviations from normal structural parameters occur, as expected, in the vicinity of the C=C bond. The dihedral angles C3-C1-C2-C5 and C4-C1-C2-C6 amount to 28.6°. The compound has a twisted conformation without any contributions from bending deformations and shows the largest twist of all purely aliphatic substituted, sterically crowded alkenes (Tables 2 and 3). The C=C bond is lengthened to 135.7 pm (ethene, 131.3 pm)<sup>26</sup> and the allylic C-C bonds to 155.5-159.7 pm (propene, 149.6 pm).† Other C-C bonds are also elongated, e.g. the C-C bonds between the quaternary and the carbonyl carbon atoms. Whereas the bond angles at the olefinic carbon atoms are only slightly changed, one tetrahedral angle in each of the four substituents is reduced to 96° (Table 2).

In the crystal all four carbonyl groups are almost parallel to a plane which bisects the molecule





Fig. 1. SCHAKAL drawings of 27: left, molecular structure and numbering of atoms in 27; right, molecular structure, view in the direction of the C=C bond.

perpendicular to the  $C_2$  axis; of the two carbonyl groups in the Z position one is located above and the other one below the C=C bond (Fig. 1).

# Attempts at the synthesis of 1 from "vicinally" bridged precursors

Thus far, only "geminally" bridged precursors, such as 8 or 22, have been considered as intermediates for the preparation of 1. In principle, "vicinally" bridged compounds, such as 11 or 12, should be equally well suited. The 3,3,6,6-tetramethyl-1-thiacycloheptyne has the required substitution pattern and, as a consequence of considerable angle bending, a high reactivity of the triple bond in addition reactions.<sup>16</sup> Addition of t-



butyllithium to 13 took place at  $-78^{\circ}$  in good (70%) yield; hydrolysis of 38 with D<sub>2</sub>O yielded 85% deuterated product and 15% 39. This shows that even at  $-78^{\circ}$  some protonation of 38 by the solvent tetrahydrofuran (THF) occurred. Since in other less polar solvents no addition of t-butyllithium was observed, THF was used in all further experiments.



Since in 38 three t-Bu groups are preformed, the fourth t-Bu group had to be introduced via a reaction with the lithiated olefinic carbon. In order to test the steric shielding of this carbon methyl iodide was used as a first reaction partner. It gave the expected product 40 in 30% yield; in addition some 39 was formed by protolysis of 38. With ethyl iodide and t-butyl chloride 38 gave only elimination and no coupling products; with trimethyliodosilane 41 was formed in very low yield (1.3%). Ethylene oxide did not react with 38 at  $-78^\circ$ , but gave only the protolysis product 39. Since in many reactions protolysis of 38 competed successfully



with the alkylation reaction, other less reactive organometallic derivatives of 38 were considered.

By reaction with copper(I) thiophenolate the cuprate 42 was prepared from 38. It is a much more stable intermediate than 38. On addition of methyl iodide 40 was isolated in 72% yield without concomitant formation of 39. Whereas reaction with ethyl iodide led only to elimination of HI and 39, addition of ethylene oxide yielded the alcohol 43. However, propylene oxide or isobutylene oxide did not give the expected products, but besides 39 the isomeric alcohols 44 and 45 in low yields.

Apparently an equilibrium exists in THF solution between 42 and 46 and in reactions with compounds larger than methyliodide or ethylene oxide only the products derived from 46 are observed. Up to now tri-tbutylmethylethylene (32) could not be prepared; on heating the thiadiazoline only cycloreversion took place and no 32 was formed.<sup>31</sup> However, on treatment



of 40 with Raney nickel 32 was obtained in 74% yield. This demonstrates that at least in this particular case addition reactions to 13 are superior to the thiadiazoline route. The even more sterically crowded hydrocarbon tri-t-butylethylethylene (33) was prepared from 43 via the mesylate 47, reduction with lithium triethylborohydride to 48 and subsequent



reductive desulfurization with Raney nickel. In addition to 33 the isomeric 49 was formed in 1% yield. From the data in Table 1 it follows that 33 is the most strained compound in this series.



According to force field calculations (MM2) the C=C bond length in 33 is 137.2 pm and the dihedral angle at the double bond is  $32.7^{\circ}$ ; this is a larger deviation from the normal structural parameters than observed in 27 by X-ray analysis.

Thus, nucleophilic addition of organolithium compounds to 13 has led to the synthesis of more highly strained alkenes, such as 33, although the ultimate aim in this series, tetrs-t-butylethylene, could not be prepared.

For this reason, the addition of alkyl radicals to 13 was investigated. Giese and Lachhein<sup>32</sup> have shown by kinetic investigations that alkyl radicals add to alkenes usually 3-5 times faster than to acetylenes. The lesser reactivity of acetylenes is explained by the higher energy of the LUMOs; however, in angle strained cycloalkynes, such as 13, the LUMO is significantly lowered.<sup>33</sup> Therefore, 13 should be a good substrate for radical addition reactions.

Since isobutyronitrile (IBN) radicals are easily generated at temperatures below 100° and represent a



bulky substituent, azoisobutyronitrile (AIBN) was thermally decomposed in the presence of 13. Two products, 50 and 51, were obtained; the formation of 50 can be explained by addition first of an IBN radical to the C—C triple bond and then attack of another IBN radical with C—N bond formation. Thermal isomerization of 50 gives 51. When the IBN radicals are generated by photolysis, the ketenimine 50 is the only product; this suggests that 51 is formed via 50.

The addition of two t-Bu radicals to 13 would in principle lead to the sterically very crowded alkene 11. However, photolysis of azo-t-butane in the presence of 13 yielded the alkene 39 (31%) and the addition product of two t-Bu radicals 46a or b. Thus, the formation of 11 was avoided for steric reasons and attack of the second t-Bu radical took place at a less hindered position leading to 46a or b.



# Attempts at the synthesis of 1 from 27

To date 27 is the precursor closest in structure to 1. Therefore, attempts at the conversion of the lour aldehyde groups into methyl groups were undertaken. Reduction of 27 with LiAlH<sub>4</sub> did not yield the expected tetraol 54, but the bis-hemiacetal 53 (47%) or an isomer.

Apparently reduction of one aldehyde group to the corresponding alcohol is followed by immediate attack of a carbonyl group leading to a very stable hemiacetal ring. Formation of 53 is favoured because strain is reduced by the formation of a cyclic structure.



Reaction of 27 with hydrazine led to two isomeric diols of structure 55 (or an isomer). The formation of these diols can be explained by a hydrazone intermediate 56, which is converted in the course of the Wolff-Kishner reduction to the carbanion 57. Internal addition to a carbonyl group leads after protonation to an alcohol 58. Thus, again formation of 1 is avoided by internal cyclization.

# Force field calculations

For some alkenes calculations were carried out using Allinger's MM2 force field. Table 4 shows fragmentation strain  $\Delta H_{fr}$ , steric energy  $\Delta H_{ster}$ , and the standard enthalpy of formation of some sterically



crowded alkenes. From a comparison of the alkenes it can be concluded that alkenes 27, 32 and 33 prepared in this work are more strained than other known related alkenes. If fragmentation strain is taken as a criterion<sup>21</sup> for achievement in the synthesis of sterically hindered alkenes, then the frontier in the direction to 1 has been pushed forward by about 73 kJ mol<sup>-1</sup> (from 31 to 27) during this work; we have still to go the same distance from 27 to 1.

Table 4. Energy parameters from MM2 force field calculations (kJ mol<sup>-1</sup>)

Alkene	$\Delta H_{\rm fr}$	$\Delta H_{\rm ster}$	ΔH°	Ref.
10	135.06	250.87	-143.10	35
31	207.99	332.08	-88.74	35
32	220.92	272.50	- 104.27	this work
33	242.21	303.72	-97.87	this work
27	281.04	375.01	-442.12	this work
Ì,	354.47	429.19	-43.68	35

### Outlook

There are still many obstacles to overcome on the route to 1; however, 27 seems to be a particularly promising milestone on the way.

### **EXPERIMENTAL**

Raman spectra were recorded on a Ramanor HG 25, Ar<sup>+</sup>-Laser (514.5 nm) and IR spectra on a Perkin-Elmer 257, 297 or 399 spectrometer. <sup>1</sup>H-NMR spectra were recorded on a Varian T 60, Bruker WH 270 or Bruker WM 400 and <sup>13</sup>C-NMR spectra on a Bruker WP 60, WP 80 or WM 400. Mass spectra were recorded on a Varian CH 7 or Finnigan 311 A spectrometer. All m.ps are uncorrected. Elemental analyses were carried out in the Microanalytical Department of the Institute of Organic Chemistry, Hamburg University.

# 2,2,5,5-Tetramethyl-3-hydroxycyclopentanone (15)

To a soln of 2,2,5,5 - tetramethyl - 1,3 - cyclopentandione<sup>19</sup> (200 g, 1.3 mol) in 0.91 THF a soln of 360 g (1.41 mol) Li(t-BuO)<sub>3</sub>AlH in 1.41 1 THF was added dropwise within 1 h at room temp, then stirred for a further 2 h. The soln was hydrolyzed with dil HCl; for a more convenient separation sat NaCl aq was added and extracted three times with ether. The combined ethereal solns were washed with sat NaHCO<sub>3</sub> aq and dried over MgSO<sub>4</sub>. After removal of the solvent 158.5 g (78%) 15 were obtained, m.p. 78°. Spectroscopic data are reported in Ref. 5.

#### 2,2,4,4 - Tetramethyl - 3 - oxocyclopentylxanthogenate

A soln of 270 ml (2 N, 0.54 mol) n-BuLi in hexane was added to 1 l of DMSO; to this soln 75.1 g (0.48 mol) 15, dissolved in 300 ml DMSO, was added dropwise within 1 h. A greenish grey soln was formed; on addition of 39 ml (0.62 mol) CS<sub>2</sub> the colour of the soln changed to dark red. The soln was stirred for 1.5 h and 41 ml (0.62 mol) CH<sub>3</sub>I added. After 2.5 h the mixture was poured into 1.4 l ico-water, stirred for 15 min and extracted three times with hexane. The hexane soln was twice treated with sat NaCl aq, dried and the solvent evaporated (15 mmHg). The resulting reddish oil (118 g) was impure xanthogenate, which was used for the pyrolysis without further purification. <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  1.13, 1.15, 1.16, 1.17 (4s, each 3H, CH<sub>3</sub>), 2.09 (q, J<sub>BX</sub> = 4.4 Hz, 2H, CH<sub>2</sub>(B)), 2.35 (q, J<sub>AX</sub> = 4.7 Hz, 2H, CH<sub>2</sub>(A)), 2.57 (s, 3H, CH<sub>3</sub>--S), 5.94 (q, CHO) ppm.

#### 2,2,5,5-Tetramethyl-3-cyclopentenone (16)

The xanthogenate (117 g, 0.45 mol) was heated slowly to 220° under a slow stream of N<sub>2</sub>. Decomposition started at 200°; product 16 was condensed into a cold trap, where it crystallized. After 5 h the xanthogenate was completely pyrolyzed and the product dissolved in pentane; the pentane was removed by slow distillation, since 16 is very volatile. Yield: 45.5 g(73%) 16, m.p. 41-43°. IR (CCL<sub>4</sub>) 1745 cm<sup>-1</sup>; <sup>1</sup>H-NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$  1.15 (s, 12H, CH<sub>3</sub>), 5.95 (s, 2H, CH) ppm; <sup>13</sup>C-NMR (15.08 MHz, CDCl<sub>3</sub>)  $\delta$  24.97 (q, CH<sub>3</sub>), 49.43 (s, C—CH<sub>3</sub>), 136.51 (d, C—C), 224.80 (s, C—O) ppm; UV (C<sub>4</sub>H<sub>12</sub>)  $\lambda_{max}$  (e) 295.5 (17) nm; MS *m/e* 138 (M<sup>+</sup>, 10%), 110 (M<sup>+</sup>-CO, 52%). (Found: C, 78.38; H, 9.97. Calc for C<sub>9</sub>H<sub>14</sub>O: C, 78.21; H, 10.21%.) Ketone 16 was also prepared according to the procedure published by Guziec and coworkers.<sup>5</sup>

# 2,2,5,5-Tetramethyl-3-cyclopentenone hydrazone (17)

Ketone 16 (69 g, 0.5 mol), hydrazine hydrate (295 ml, 5.9 mol) in diethylene glycol (1.5 l) and EtOH (20 ml) were heated to reflux under N<sub>2</sub> for 72 h. The cooled soln was diluted with 750 ml NaCl soln and extracted with ether (4 × 500 ml). The ether extract was washed with sat NaCl aq, dried and the solvent removed under reduced pressure. Yield: 66.2 g (87%), m.p. 72-74° (hexane). IR (CCl<sub>4</sub>) 3400 (NH), 1660 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$  1.16 (s, 6H, CH<sub>3</sub>), 1.42 (s, 6H, CH<sub>3</sub>), 5.52 (AB, J<sub>AB</sub> = 6 Hz, 2H, CH) ppm; <sup>13</sup>C-NMR (20.14 MHz, CDCl<sub>3</sub>) 28.98 (q, CH<sub>3</sub>), 28.52 (q, CH<sub>3</sub>), 46.49 (s, <u>C</u>-CH, 1.48 491; <u>C</u>-CH<sub>3</sub>), 136.92 (d, C=C), 137.10 (d, C=C), 165 79 (s, C=N) ppm, UV (n-hexane)  $\lambda_{max}$  (s) 212 (2200) nm; MS m/e 152 (M<sup>+</sup>, 30%), 137 (M<sup>+</sup>-CH<sub>3</sub>), 100%).

#### 4-Diazo-3,3,5,5-tetramethylcyclopentene (18)

To a soln of 12 g (79 mmol) 17 in 400 ml petroleum ether (30– 50°) 48 g nickel peroxide was added at 0° and stirred for 3 h at 0°. After 1 h at room temp the nickel oxides were removed by filtration and the solvent removed at reduced pressure. The red diazoalkene was used immediately for the next reaction to avoid decomposition. Yield: 10.6 g (90%). IR (CCl<sub>4</sub>) 2045 (C=N<sub>2</sub>) cm<sup>-1</sup>; UV-vis  $\lambda_{max}(e)$  192 (3700), 232 (4650), 501 (2.5) nm.

# 2,2,5,5-Tetramethyl-3-cyclopentenethione (19)

To a cooled (0°) soln of 50 ml (0.33 mol) Et<sub>3</sub>N in 11 petroleum ether (30–50°) a soln of 25 g (0.165 mol) 17 in 250 ml petroleum ether and a soln of 13 ml (0.165 mol)  $S_2Cl_2$  in 250 ml petroleum ether was added simultaneously from two dropping funnels within 1 h. After 3 h the ppt was filtered off, the pink soln washed neutral and most of the solvent removed at reduced pressure. After 12 h precipitated sulfur was separated and the crude product purified by column chromatography on 300 g silica gel with petroleum ether. Yield: 17.6 g (69%), mp. 48–51°. IR 1625 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$ 1.23 (s, 12H, CH<sub>3</sub>), 5.95 (s, 2H, CH) ppm; <sup>13</sup>C-NMR (20.14 MHz, CDCl<sub>3</sub>) & 30.08 (q, CH<sub>3</sub>), 61.98 (s, C—CH<sub>3</sub>), 136.60 (d, C—C), 282.20 (s, C=S) ppm; UV-vis (n-becane)  $\lambda_{max}$  (e) 209 (8550), 225 (12,200), 260 (4100), 491 (8) nm; MS m/e 154 (M<sup>+</sup>, 35%), 139 (M<sup>+</sup> - CH<sub>3</sub>, 100%). (Found: C, 70.24; H, 9.13; S, 20.65. Calc for C<sub>8</sub>H<sub>1</sub>, S: C, 70.07; H, 9.15; S, 20.78%.)

1,1,4,4,8,8,11,11 - Octamethyl - 6 - thia - 12,13 diazadispiro(4.1.4.2)trideca - 2,9,12 - triene (28)

Thione 19 (6 g, 39 mmol) and 18 (5.83 g, 39 mmol), each dissolved in 200 ml petroleum other (30–50°) were mixed at 0°. After 3 h at 0° the soln was discoloured and subsequently the solvent removed at reduced pressure. Yield: 10.1 g (83%). Decomposition of 20 occurs near 125°. IR (KBr) 1640 (C=C), 1575 (N=N) cm<sup>-1</sup>; <sup>1</sup>H-NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$  0.98 (s, 12H, CH<sub>3</sub>), 1.23 (s, 12H, CH<sub>3</sub>), 5.43 (s, 4H, CH) ppm; <sup>13</sup>C-NMR (20.14 MHz, CDCl<sub>3</sub>)  $\delta$  23.75 (q, CH<sub>3</sub>), 30.11 (q, CH<sub>3</sub>), 54.32 (s, C=CH<sub>3</sub>), 124.37 (a, C=S), 137.31 (d, C=C) ppm; UV-vis (n-hexane)  $\lambda_{max}$  (e) 205 (2070), 283 (1030), 333 (312) nm; MS m/e 289 (M<sup>+</sup> - CH<sub>3</sub>, S<sup>\*</sup>, 10° c, 10° c) (Found: C, 70.76; H, 9 21, N, 9 21, S, 10 59. Calc for C<sub>18</sub>H<sub>28</sub>N<sub>2</sub>S C, 71.00; H, 9 27, N, 9 20, S, 10.53° i

1,1,4,4,8,8,11,11 - Octamethyl - 6 - thiadispiro(4.0.4.1)undeca - 2,9 - diene (21)

A flask containing 10 g (33 mmol) 20 was immersed in a bath kept at 140°. The compound melted immediately and was thermolyzed for 30 min; volatile decomposition products were removed at reduced pressure (1 mm Hg). The crude product was purified by chromatography on silica gel with petroleum ether (60-70°). Yield: 7.3 g (79%), m.p. 132°. IR (KBr) 1680 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$  1.28 (a, 12H, CH<sub>3</sub>), 1.53 (a, 12H, CH<sub>3</sub>), 5.35 (a, 4H, CH) ppm; <sup>13</sup>C-NMR (20.14 MHz, CDCl<sub>3</sub>)  $\delta$  31.18 (q. CH<sub>3</sub>), 52.79 (a, C —CH<sub>3</sub>), 78.63 (a, C=S), 138.85 (d, C=C) ppm; UV (n-hexane)  $\lambda_{max}$  (e) 200 (2570), 265 (120) nm; MS m/e 276 (M<sup>+</sup>, 3.5%). (Found: C, 78.45; H, 10.25; S, 11.89. Calc for C<sub>18</sub>H<sub>28</sub>S: C, 78.20; H, 10.21; S, 11.60%)

#### Bi-3,3,5,5-tetramethylcyclopenten-4-ylidene (22)

Method A. Thiirane 21 (15.6 g, 56.7 mmol) was heated in  $(n-Bu)_{3}P$  (46 g, 0.23 mol) at 140°. To the cooled mixture 250 ml petroleum ether (60–70°) and subsequently 20 ml (0.32 mol) MeI were added and stirred overnight. The ppt was filtered off, washed with H<sub>2</sub>O and the solvent removed. Chromatography (silica gel, petroleum ether 60–70°) and recrystallization from MeOH afforded pure 22. Yield : 9.4 g (68%), m.p. 108°.

Method B. A mixture of 554 mg(1.82 mmol) 20 and 2.63 g(13 mmol)(n-Bu)<sub>3</sub> P was immersed in a bath kept at 130° for 2 h. To the cooled mixture 4 ml MeI in 20 ml petroleum ether was added. Further purification as in Method A. Yield: 316 mg (71%). IR (KBr) 1660 (C=C) cm<sup>-1</sup>; Raman (crystal, 514.5 nm) 1663 (C=C), 1563, 1536 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$  1.45 (a, 24H, CH<sub>3</sub>), 5.16 (a, 4H, C=C-H); <sup>13</sup>C-NMR (20.14 MHz, CDCl<sub>3</sub>)  $\delta$  31.02 (q, CH<sub>3</sub>), 51.98 (a, C-C-H<sub>3</sub>), 138.06 (d, CH=CH), 151.27 (s, C=C) ppm; UV (C<sub>6</sub>H<sub>12</sub>)  $\lambda_{max}$  (e) 219.6 (3350) nm; MS m/e 244 (M<sup>+</sup>, 95%). (Found: C, 87.98; H, 11.36. Calc for C<sub>18</sub>H<sub>28</sub>; C, 88.45; H, 11.54%.)

#### 2,2,2',2',5,5,5',5' - Octamethyl - 3,3',4,4' - tetrahydroxy - 1,1' bicyclopentylidene (23)

To a soln of OsO<sub>4</sub> (4.22 g, 16.6 mmol) in 10ml pyridine a soln of 22(1.98 g, 8.1 mmol) in 40 ml ether-pyridine (4:1) was added dropwise over the course of 12 days. The reaction was stopped when all 22 and OsO<sub>4</sub> had reacted. The mixture was diluted with 200 ml ether under N<sub>2</sub> and stirred overnight with LiAlH<sub>4</sub> (2.5 g, 65 mmol). Refluxing for 3 h completed the reduction yielding a black soln; the soln was cooled to 0°, hydrolyzed carefully with H<sub>2</sub>O (5 ml) and, after H<sub>2</sub> evolution had ceased, refluxed for 5 h. The ether soln was decanted from the ppt, treated three times with 2 N HCl, once with H<sub>2</sub>O, once with MaCl aq, dried over MgSO<sub>4</sub> and concentrated at reduced pressure. The resulting mixture (1.6 g) was chromatographed

on silica gel (200 g) with EtOAo-petroleum ether to yield 1.03 g (41%) 23 (m.p. 205") and 0.27 g (12%) 24 (m.p. 162-163").

Spectroscopic data of 23. IR (KBr) 3420 (OH) cm<sup>-1</sup>; <sup>1</sup>H-NMR (270 MHz, d<sub>6</sub>-DMSO)  $\delta$  1.29 (s, 12H, CH<sub>3</sub>), 1.38 (s, 12H, CH<sub>3</sub>) 23a; 1.31 (s, 12H, CH<sub>3</sub>), 1.37 (s, 12H, CH<sub>3</sub>) 23b; 3.43 (d, 4H, CH—O), 4.33 (d, 4H, OH) ppm 23a+23b, <sup>13</sup>C-NMR (20.15 MHz, CD<sub>3</sub>OD)  $\delta$  26.11 (q, CH<sub>3</sub>), 32.19 (q, CH<sub>3</sub>), 83.09 (d, CHOH), 48.78 (s, Cq), 153.10 (s, C=C) ppm; MS m/e 312 (M<sup>+</sup>, 50%). (Found: C, 68.79; H, 10.05. Calc for C<sub>19</sub>H<sub>32</sub>O<sub>4</sub>: C, 69.19; H, 10.32%.)

Spectroscopic data of 24. IR (KBr) 3500–3300 (OH), 1630 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (270 MHz, d<sub>6</sub>-DMSO)  $\delta$  1.28, 1.36, 1.37, 1.39(4s, each 6H, CH<sub>3</sub>), 3.43(s, 2H, CH<sub>-</sub>OH), 4.33(s, 2H, OH), 5.11 (s, 2H, HC=CH) ppm; <sup>13</sup>C-NMR (15.08 MHz, CD<sub>3</sub>OD)  $\delta$  26.36(q, CH<sub>3</sub>), 31.71 (q, CH<sub>3</sub>), 32.10(q, CH<sub>3</sub>), 49.29 (s, Cq), 52.72 (s, Cq), 82.68 (d, CHO), 138.50 (d, CH=CH), 152.40 (s, C=C) ppm; MS m/e 278 (M<sup>+</sup>, 13%). (Found: C, 75.06; H, 10.73. Calc for C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>  $\cdot$  0.5H<sub>2</sub>O: C, 75.19; H, 10.52%.)

# 3,3,6,6,8,8 - Hexamethyl - 7 - (2',2',5',5' - tetramethylcyclopent -3 - ene - 1 - ylidene) - 2,4 - dioxabicyclo(3.3.0)octane (25)

Diol 24 (77.8 mg 0.28 mmol) was dissolved in 2 ml MeOH and 2 ml 2-methoxypropene; a violent reaction occurred. MeOH and excess methoxypropene were removed and the residue purified by chromatography (silica gel, petroleum ether-EtOAc 1:1). Yield: 70 mg (80%) 25, mp. 75-80°. IR (KBr) 1680 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta$  1.20, 1.33 (2s, each 3H, CH<sub>3</sub>), 1.36 (s, 12H, CH<sub>3</sub>), 1.40 (s, 12H, CH<sub>3</sub>), 3.90 (s, 2H, HCO), 4.95 (s, 2H, CH=CH) ppm; MS *m/e* 318 (M<sup>+</sup>, 11%).

3,3,6,6,8,8 - Hexamethyl - 7 - (2',2',5',5') - tetramethyl - 3,4 - dihydroxycyclopentylidene) - 2,4 - dioxabicyclo(3.3.0)octane (26)

To ketal 25 (65 mg, 0.2 mmol) in 5.5 ml ether  $OsO_4$  (70 mg, 0.28 mmol) was added. After 5 weeks at room temp the reaction was complete; work up as in the synthesis of 23. Yield: 60 mg 26 (83%). IR (KBr) 3500–3300 (OH) cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta$  1.32 (s, 3H, CH<sub>3</sub>), 1.365 (s, 6H, CH<sub>3</sub>), 1.370 (s, 6H, CH<sub>3</sub>), 1.45 (s, 3H, CH<sub>3</sub>), 1.48 (s, 6H, CH<sub>3</sub>), 1.51 (s, 6H, CH<sub>3</sub>), 2.22 (m, 2H, OH), 3.53 (s, 2H, CHO), 3.89 (s, 2H, CHO) ppm; MS *m/e* 352 (M<sup>+</sup>, 13%). Ketaldiol 26 (4.4 mg, 0.0125 mmol) in 1 ml CH<sub>3</sub>OH, 0.5 ml H<sub>2</sub>O and 3 drops of CF<sub>3</sub>COOH was stirred for 4 h at room temp. After removal of the solvents 3.5 mg(89%) of 23 was obtained.

#### Tetrakis(2-formyl-2-propyl)ethylene (27)

Method A. A mixture of 23 (0.84 g, 2.69 mmol) and NaIO<sub>4</sub> (1.2 g, 5.6 mmol) in 75 ml THF and 50 ml H<sub>2</sub>O was stirred for 2 h and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 ×). The extracts were dried over MgSO<sub>4</sub> and the solvent removed. Chromatography with petroleum ether-EtOAc gave three main fractions: fraction 1, 214.6 mg (26%) 27, m.p. 140° (dec.) (CH<sub>3</sub>OH or CH<sub>3</sub>CN); fraction 2, 302.3 mg (36%) 28; fraction 3, 173.5 mg (20.5%) 23.

Spectroscopic data of **27**. IR (KBr) 1730 (C=O) cm<sup>-1</sup>; Raman (514.5 nm) 1736, 1715 (C=O), 1461 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (270 MHz,  $d_6$ - $C_6H_6$ )  $\delta$  1.20 (s, 24H, CH<sub>3</sub>), 9.18 (s, 4H, CHO) ppm; <sup>13</sup>C-NMR (20.15 MHz, CDCl<sub>3</sub>)  $\delta$  25.47 (q, CH<sub>3</sub>), 56.16 (s, Cq), 150.17 (s, C=C), 199.09 (d, CHO) ppm; MS m/e 308 (M<sup>+</sup>, 0.1%); UV (C<sub>6</sub>H<sub>12</sub>)  $\lambda_{max}$  (s) 207 (2150), 241 (1500) nm. (Found: C, 70.12; H, 9.00. Calc for C<sub>18</sub>H<sub>28</sub>O<sub>4</sub>: C, 70.07; H, 9.15%)

Spectroscopic data of **28**. IR 3420 (OH), 1730 (C=O) cm<sup>-1</sup>; <sup>1</sup>H-NMR (270 MHz, d<sub>6</sub>-acetope)  $\delta$  1.12, 1.23, 1.35, 1.45 (4s, each 6H, CH<sub>3</sub>), 2.80 (2H, OH), 3.57 (s, 2H, CHO), 9.53 (s, 2H, HC=O) ppm; <sup>13</sup>C-NMR (100.62 MHz, d<sub>8</sub>-benzene)  $\delta$  24.95 (q, CH<sub>3</sub>), 26.39 (q, CH<sub>3</sub>), 49.20 (s, Cq), 54.72 (s, Cq), 60.11 (d, C=O), 137.88 (s, C=C), 161.81 (s, C=C), 203.50 (d, C=O) ppm; MS m/e 310 (M<sup>+</sup>, 1.2%).

Method B (ozonization). In 600 ml EtOAc 3.0 g (12.27 mmol) triene 22 and 3.13 g (24.45 mmol) tetracyanoethylene were dissolved and the mixture under  $N_2$  was cooled to  $-78^\circ$ ; on cooling some turbidity of the soln was observed. Ozone was

bubbled through the soln (30 min) until the turbidity disappeared. After removal of the solvent chromatography yielded 2.18 g (57%) 27.

# Tetrahydro - 2,2,2',2',6,6,6',6' - octamethyl - 3,3' - dihydroxy -4H - 1,1' - bipyranylidene (53)

To a soln of 520 mg (13.7 mmol) LiAlH<sub>4</sub> in 150 ml THF a soln of 2.0 g(6.5 mmol) 27 in 150 ml THF was added within 1 b at 0° and then stirred for a further 15 h at room temp. A H<sub>2</sub>O-THF (1:3) soln (21 ml) was used for hydrolysis. After filtration the organic phase was diluted with 100 ml ether, washed with H<sub>2</sub>O (2×) and NaCl soln and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent at reduced pressure a residue (1.7 g) was obtained, which was separated by column chromatography (silica gel; petroleum ether-EtOAc). Yield: 950 mg (47%) 47, m.p. 180° (EtOAc-n-heptane).

Spectroscopic data **53**. IR (KBr) 3350 (OH) cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$  1.09 (a, 6H, CH<sub>3</sub>), 1.20 (a, 6H, CH<sub>3</sub>), 1.26 (m, 6H, CH<sub>3</sub>), 1.43 (m, 6H, CH<sub>3</sub>), 3.03 (d, J<sub>AB</sub> = 12 Hz, 2H, CH<sub>2</sub>(B)), 3.33 (d, 2H, CH<sub>2</sub>(A)), 4.73 (d, 2H, CH-O), 6.36 (m, 2H, OH) ppm; <sup>13</sup>C-NMR (100.62 MHz, d<sub>8</sub>-THF, J-Modul)  $\delta$ 14.32 (CH<sub>2</sub>), 27.75 (CH<sub>3</sub>), 32.76 (CH<sub>2</sub>), 43.95 (Cq1 49.00 (Cq), 100.46 (CH-O), 150.53 (C=C) ppm MS  $m_1$ , 312 (M<sup>+</sup>, 0.14°<sub>0</sub>). (Found: C, 69.34; H, 10.56. Calc for C<sub>18</sub>H<sub>32</sub>O<sub>4</sub>: C, 69.19; H, 10.32%)

### Reaction of 27 with hydrazine

A soln of 600 mg (1.95 mmol) 27 in 10 ml EtOH and 5 ml (157 mmol) N<sub>2</sub>H<sub>4</sub> was heated. At 60-70° reaction occurred (evolution of gas); the mixture was refluxed for 2 h and then the solvent and excess hydrazine removed. After chromatography (slica gel, EtOAc-petroleum ether 2:3) 370 mg (68%) of 55 were obtained. IR (KBr) 3450-3400 (OH) cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, d<sub>6</sub>-acetone)  $\delta$  1.025, 1.20, 1.33, 1.38 (48, each 6H, CH<sub>3</sub>), 1.53 (q, J<sub>BX</sub> = 9.0 Hz, 2H, CH<sub>2</sub>(B)), 1.75 (t, J<sub>AX</sub> = 8.7 Hz, 2H, CH<sub>2</sub>(A)), 3.59 (q, J<sub>AB</sub> = 11.6 Hz, 2H, CH—O(X)), 3.60 (s, 2H, OH) ppm; <sup>13</sup>C-NMR (100 62 MHz, d<sub>6</sub>-acetone)  $\delta$  2.2 21, 31.08, 32.65, 33.87 (all q, CH<sub>3</sub>), 41 651x, Cqi, 49 7715, Cqi, 52 60 (t, CH<sub>2</sub>), 78.47 (d, CHOH), 152.86 (s, C=C) ppm, MS *m* e 280 (M<sup>+</sup>, 30%). (Found: C, 72.68, H, 10.92 Calc for C<sub>18</sub>H<sub>32</sub>O<sub>3</sub>·H<sub>2</sub>O: C, 72.44; H, 11.48%)

4-t-Butyl-3,3,6,6-tetramethyl-1-thia-4-cycloheptene (39) To a soln of 0.58 g (3.5 mmol) 13 in 20 ml abs THF 2.5 ml (3.5 mmol) t-BuLi (1.4 M in pentane) under N<sub>2</sub> was added at  $-78^{\circ}$ ; the mixture was kept at  $-78^{\circ}$  for 1 h and then hydrolyzed. At room temp 30 ml hexane were added, the soln washed with 50 ml H<sub>2</sub>O (2 ×) and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the product purified by column chromatography (silica gel, petroleum ether-CH<sub>2</sub>Cl<sub>2</sub> 3:1). Yield: 550 mg (70%) 39. <sup>1</sup>H-NMR (270 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.11, 1.29 (2s, each 6H, C(CH<sub>3</sub>)<sub>2</sub>), 1.14 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 2.43, 2.55 (2s, each 2H, CH<sub>2</sub>S), 5.34 (s, 1H, H-C=); <sup>13</sup>C-NMR (20.15 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  31.09 (q, C(CH<sub>3</sub>)<sub>2</sub>), 31.67 (q, C(CH<sub>3</sub>)<sub>3</sub>), 33.64 (q, C(CH<sub>3</sub>)<sub>2</sub>), 39.99, 43.34, 47.85 (35, Cq), 42.64, 48.62 (2t, CH<sub>2</sub>S), 135.58 (d, H-C=), 151.55 (s, C=); MS m/e 170 (M-C<sub>4</sub>H<sub>8</sub>, 68.8%). (Found: C, 74.88; H, 11.53; S, 14.35. Calc for C<sub>14</sub>H<sub>26</sub>S: C, 74.77; H, 11.57; S, 14.16%.)

4-t-Butyl-3,3,5,6,6-pentamethyl-1-thia-4-cycloheptene (40) To a soln of 4.38 g(26 mmol) 13 in 100 ml abs THF 20 ml (28 mmol) t-BuLi (1.4 M in pentane) was added at  $-78^{\circ}$  and the mixture stirred for 45 min. Then 8.51 g (60 mmol) MeI was added. After 10 min cooling was discontinued and after 1 h at room temp the mixture was bydrolyzed, 100 ml hexane added and washed with H<sub>2</sub>O (2 × ). The soln was dried over Na<sub>2</sub>SO<sub>4</sub> and then the solvent removed. The crude product was chromatographed (silica gel, petroleum ether-CH<sub>2</sub>Cl<sub>2</sub> 3:1). Yield: 1.82 g (30%) 40, m.p. 51°. Raman (514.5 nm) 1533.6 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, d<sub>3</sub>-nitrobenzene, 140°) 1.26 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.35 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.44 (s, 3H, C(CH<sub>3</sub>)<sub>2</sub>), 1.85 (s, 3H, CH<sub>3</sub>), 2.45 (s, 2H, CH<sub>2</sub>S). 2.49 (s, 2H, CH<sub>3</sub>S) ppm; <sup>13</sup>C-NMR (20.15 MHz, CDCl<sub>3</sub>)  $\delta$  22.22, 31.51, 33.42, 34.41 (CH<sub>3</sub>), 39.59, 43.75, 43.98 (Cq), 40.38, 45.78  $(CH_2-S)$ , 143.31, 150.50 (C=C) ppm; MS m/e 225 (M<sup>+</sup> -CH<sub>3</sub>, 0.27%). (Found : C, 74.89; H, 11.61; S, 13.60. Calc for C<sub>15</sub>H<sub>28</sub>S: C, 74.93; H, 11.74; S, 13.33%.)

# 4 - t - Butyl - 5 - (2 - hydroxyethyl) - 3,3,6,6 - tetramethyl - 1 - thia - 4 - cycloheptene (43)

To a soln of 5.04 g (30 mmol) 13 in 100 ml abs THF 25 ml (30 mmol) t-BuLi (1.2 M in pentane) was added at  $-78^4$ , stirred for 30 min and then a soln of 30 mmol copper thiophenolate<sup>36</sup> in 50 ml abs THF added dropwise within 15 min. After a further 10 min 2.64 g (60 mmol) ethylene oxide was added. Cooling was discontinued and it stirred overnight. Hexane(100 ml) and then H<sub>2</sub>O (20 ml) was added. A ppt was removed by filtration over Celite, the filtrate washed with water (3 ×), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent evaporated. After chromatography (petroleum ether-ether 1 : 1) pure 43 was obtained. Yield : 3.20 g (40%) 43, m.p. 118° (hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, -20°)  $\delta$  1.18, 1.28, 1.36, 1.54 (4s, each 3H, CH<sub>3</sub>), 1.28 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.89 (d, J<sub>AB</sub> = 14.2 Hz, 1H, CH<sub>2</sub>S), 2.02 (d, J<sub>AB</sub> = 14.2 Hz, 1H, CH<sub>2</sub>S), 2.02 (d, J<sub>AB</sub> = 14.2 Hz, 1H, CH<sub>2</sub>S), 2.02 (d, J<sub>AB</sub> = 14.2 Hz, 1H, CH<sub>2</sub>S), 2.03 (broad signal, 1H, OH), 5% 3.10, 3.31, 3.60 (4m, 4H, CH<sub>2</sub>-CH<sub>2</sub>OH) ppm. MS *m/e* 255 (M - CH<sub>3</sub>, 0.38%). (Found : C, 71.28; H, 11.29; S, 12.10. Calc for C<sub>16</sub>H<sub>30</sub>OS: C, 71.05; H, 11.18; S, 11.85%)

#### Mesylate of 43 (47)

To a soln of 1.5 g(5.56 mmol) 43 in 30 ml CH2Cl2 were added 0.8 g (8 mmol) Et<sub>3</sub>N and 0.64 g (5.6 mmol) CH<sub>3</sub>SO<sub>2</sub>Cl at 0°. After addition the ice bath was removed and the mixture stirred for 40 min at room temp. Ether (50 ml) was added, the soln washed with 50 ml H<sub>2</sub>O, with 50 ml 10% HCl aq  $(2 \times)$  and again with 50 ml  $H_2O(2 \times)$  and then dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent 1.9 g of light yellow crystals remained, which were recrystallized from 150 ml hexane. Yield: 1.75 g(90%) 47, m.p. 104°. IR (KBr) 1480 (C==C) cm<sup>--</sup> UV (C6H12) Amax (e) 251 (2600), 237 (2600) nm; 1H-NMR (400 MHz, C6D6) 80.84, 0.99, 1.29, 1.47 (4s, each 3H, CH3), 1.17 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.62 and 2.62 (AB system,  $J_{AB} = 14.2$  Hz, 2H, CH<sub>2</sub>S), 1.71 and 2.77 (AB system,  $J_{AB} = 14.2$  Hz, 2H, CH<sub>2</sub>S), 1.71 and 2.77 (AB system,  $J_{AB} = 14.2$  Hz, 2H, CH<sub>2</sub>S), 2.23 (s, 3H, SO<sub>2</sub>CH<sub>3</sub>), 2.63, 3.24, 3.78, 4.09 (4m, each 1H, CH<sub>2</sub>—CH<sub>2</sub>—O) ppm; <sup>13</sup>C-NMR (100.62 MHz, CDCl<sub>3</sub>)  $\delta$ 24.13, 25.73, 34.60, 37.58, 39.35 (5q, CH<sub>3</sub>), 35.00 (q, C(CH<sub>3</sub>)<sub>3</sub>), 35.81 (t, =C-<u>C</u>H<sub>2</sub>), 39.35, 45.84 (2t, CH<sub>2</sub>-S) 39.94, 44.95, 45.07 (3s, Cq), 70.77 (t, CH2O), 142.77, 154.38 (2s, C=) ppm; MS (CI) m/e 349 (M+1, 8%). (Found : C, 58.69; H, 9.43; S, 18.48. Calc for C17H32S2O3: C, 58.58; H, 9.25; S, 18.40%)

#### 4 - t - Butyl - 5 - ethyl - 3,3,6,6 - tetramethyl - 1 - thia -4-cycloheptene (48)

To a soln of 1.4 g (4 mmol) 47 in 30 ml THF 5 ml (5 mmol), LiB(C2H3)3H (1.0 M in THF) was added and stirred for 5 h at room temp. Hexane (50 ml) was added, washed with  $H_1O(2 \times)$ and dried over Na2SO4. The solvent was evaporated and the residue purified by chromatography (silica gel, petroleum ether-CH<sub>2</sub>Cl<sub>2</sub> 5:1). Yield: 780 mg (77%) 48, m.p. 123° (MeOH). IR (KBr) 3030, 3000 (CH<sub>3</sub>, CH<sub>2</sub>) cm<sup>-1</sup>; Raman (514.5 nm) 1503 (C=C) cm<sup>-1</sup>; UV (C<sub>6</sub>H<sub>12</sub>)  $\lambda_{max}$  (a) 210(4500), 225 (3400), 251 (3800) nm; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 0°) δ 0.95(t, J = 7.4 Hz, 3H, CH2CH3), 1.14, 1.29, 1.36, 1.55(4s, each 3H, CH<sub>3</sub>), 1.33 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.87, 2.98 (AB system, J<sub>AB</sub> = 13.4 Hz, 2H, CH<sub>2</sub>S), 2.16, 3.01 (AB system,  $J_{AB}$  = 13.4 Hz, 2H, CH<sub>2</sub>S), 2.27, 2.88 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>) ppm; <sup>13</sup>C-NMR (100.62 MHz, CDCl<sub>3</sub>) δ 19.01 (q, CH<sub>2</sub>CH<sub>3</sub>), 24.37, 25.83, 32.30, 33.85 (4q, CH<sub>3</sub>), 28.73 (t, CH<sub>2</sub>CH<sub>3</sub>), 35.10 (q, C(CH<sub>3</sub>)<sub>3</sub>), 39.54, 44.16, 45.04 (3s, Cq), 39.54, 45.24 (2t, CH2S), 147.41, 152.84 (2s, C=) ppm; MS m/e 239 (M-CH, 0.4%), 198 (M-C<sub>4</sub>H<sub>s</sub>, 30%) (Found C. 75.66; H, 11.82: S. 12.50. Calc for C, H, S: C, 75.52; H, 11.88; S, 12.60%.)

#### Tri-t-butylethylethylene (33)

Raney Ni<sup>38</sup> was prepared from 25 g Ni-Al alloy and washed three times with abs dioxane under N<sub>2</sub>, then 50 ml abs dioxane were added. To this slurry a soln of 540 mg (2.13 mmol) 48 in 50 ml abs dioxane was added, the mixture refluxed for 24 h, decanted from Ni and washed three times with hot dioxane. After evaporation of the solvent at reduced pressure 250 mg of a colourless liquid was obtained, which was purified by column chromatography (silter gel, hexane) and subsequently by preparative VPC (10% OV 101, 180° isotherm). Yields: 91.9 mg (20%) 33, m.p. 73° (CH<sub>3</sub>CN); 5.7 mg (1%) 49.

Spectroscopie data of 33. HK (CCl<sub>4</sub>) 3060, 3040 (CH<sub>2</sub>, CH<sub>2</sub>) cm<sup>-1</sup>; Reman (514.5 nm) 1475(C=C) cm<sup>-1</sup>; UV (C<sub>6</sub>H<sub>12</sub>)  $\lambda_{max}$ (e) 245 (3700) nm; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) § 0.94 (t, J = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.24, 1.30, 1.34 (3e, each 3H, C(CH<sub>3</sub>)<sub>3</sub>), 2.57 (q, J = 7.4 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>) ppm; <sup>13</sup>C-NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>) § 18.34 (q, CH<sub>3</sub>), 31.14 (t, CH<sub>2</sub>), 30.22, 33.48, 44.66 (3e, C(CH<sub>3</sub>)<sub>3</sub>), 33.65, 34.96, 35.30 (3q, C(CH<sub>3</sub>)<sub>3</sub>), 152.15, 154.45 (2z, C=) ppm; MS m/e 224 (M<sup>+</sup>, 4%). (Found: C, 85.48; H, 14.40. Calc for C<sub>16</sub>H<sub>32</sub>: C, 85.62; H, 14.37%) Spectroscopic data of 49. <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) 1.05

Spectroscopic data of 49. <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) 1.05 (s, 18H,  $2 \times C(CH_3)_3$ ), 1.22(s, 9H,  $C(CH_3)_3$ ), 1.85(d, J = 7.6 Hz, 3H, =-CH--C<u>H\_3</u>), 2.23 (s, 1H, CH), 5.38 (q, J = 7.6 Hz, 1H, =-CH) ppm; <sup>13</sup>C-NMR (100.62 MHz, CDCl<sub>3</sub>) 16.22 (q, CH<sub>3</sub>), 22.98 (q,  $C(CH_3)_3$ ), 32.48 (q,  $2 \times C(CH_3)_3$ ), 37.73 (s,  $2 \times C(CH_3)_3$ ), 44.61 (s,  $C(CH_3)_3$ ), 57.33 (d, <u>CH</u>), 121.78 (d, =-CH), 160.09 (s, C=) ppm; MS *m/e* 224 (M<sup>+</sup>, 3.4%).

#### Tri-t-butylmethylethylene (32)

Raney Ni was prepared from 10 g NiAl alloy (50%, 85 mmol Ni) and NaOH and washed three times with abs dioxane under N<sub>2</sub>. Then 180 mg (0.75 mmol) 40 in 30 ml dioxane were added to the Raney Ni slurry and refluxed for 17 h. After cooling the soln was decanted, the Ni washed three times with hot dioxane and the solvent evaporated. Yield: 116.6 mg (74%) 32, colourless liquid. IR (film) 3070, 3040, 3020 (CH<sub>3</sub>, CH<sub>2</sub>) cm<sup>-1</sup>; Raman (514.5 nm) 1516 (C=C) cm<sup>-1</sup>; UV (C<sub>6</sub>H<sub>12</sub>)  $\lambda_{mex}$  (2) 234 (5000) nm; <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.23, 1.35, 1.38 (3s, each 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.76 (s, 3H, CH<sub>3</sub>), 32.29, 34.43, 35.20 (3q, C(CH<sub>3</sub>)<sub>3</sub>), 40.19, 40.36, 41.35 (3s, C(CH<sub>3</sub>)<sub>3</sub>), 145.59, 152.96 (2s, C==); MS m/e 210 (M<sup>+</sup>, 4.7%). (Found : C, 85.67; H, 14.40. Calc for C<sub>15</sub>H<sub>30</sub>: C, 85.63; H, 14.37%.)

Addition of isobutyronitrile radicals to 13: 2,2,6,6,10,10 hexamethyl - 9 - (1 - cyano - 1 - methylethyl) - 8 - aza - 4 thiabicyclo[5.3.0]deca - 1(7),8 - diene (51) and 3,3,6,6 tetramethyl - 4 - (1 - cyano - 1 - methylethyl) - 5 - (3 - methyl - 1 aza - 1,2 - butadienyl) - 1 - thia - 4 - cycloheptene (50)

(a) Thermal generation of IBN radicals. Under  $N_2$  336 mg (2 mmol) 13 and 328 mg (2 mmol) azoisobutyronitrile (AIBN) in 15 ml abs benzene were refluxed for 6 h; after this time the evolution of  $N_2$  had ceased. Two products were detected by TLC and were separated by column chromatography (silica gel, petroleum ether-ether 10: 1). Yield: 310 mg (51%) 51, m.p. 100° (hexane); 240 mg (39%) 50, m.p. 83° (MeOH).

Spectroscopic data of 51. IR (KBr) 2235 (C=N), 1685 (C=N) cm<sup>-1</sup>; UV (C<sub>6</sub>H<sub>12</sub>)  $\lambda_{max}$  (e) 230 (1220), 244 (1090), 276 (1250) nm; <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.14, 1.15, 1.48, 1.49 (44, each 6H, C(CH<sub>3</sub>)<sub>2</sub>), 2.33, 2.41 (2s, 2H, CH<sub>2</sub>S) ppm; <sup>13</sup>C-NMR (100.62 MHz, CDCl<sub>3</sub>)  $\delta$  25.47, 25.53, 27.15, 31.07 (4q, C(CH<sub>3</sub>)<sub>2</sub>), 40.20, 42.93, 50.69, 59.50 (4s, C(CH<sub>3</sub>)<sub>2</sub>), 49.29, 50.30 (2t, CH<sub>2</sub>S), 125.31 (s, C=N), 147.28 (s, C=), 167.19, 169.16 (2s, C=N and =C-N) ppm; MS *m/e* 304 (M<sup>+</sup>, 66.6%), 236 (M -C<sub>4</sub>H<sub>6</sub>N, 97.7%), 180 (M - C<sub>4</sub>H<sub>6</sub>N - C<sub>4</sub>H<sub>8</sub>, 80%). (Found: C, 70.73; H, 9.27; N, 9.06; S, 10.51. Calc for C<sub>18</sub>H<sub>28</sub>N<sub>2</sub>S: C, 71.00; H, 9.27; N, 9.20; S, 10.53%.)

Spectroscopic data of **50**. IR (KBr) 2240 (C=N), 1995 (C=C=N) cm<sup>-1</sup>; Raman (514.5 nm) 2236 (C=N), 1990 (C=C=N) cm<sup>-1</sup>; UV (C<sub>6</sub>H<sub>12</sub>)  $\lambda_{max}$  (e) 214 (10,800) nm; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) 2 isomers (I and II) in a ratio 5:2, isomer I  $\delta$  1.15, 1.24, 1.29, 1.51, 1.60, 1.68, 1.75, 1.93 (88, each 3H, CH<sub>3</sub>), 2.21, 3.51 (AB system, J<sub>AB</sub> = 14.6 Hz, 2H, CH<sub>2</sub>S), 2.43, 2.64 (AB system, J<sub>AB</sub> = 13.2 Hz, 2H, CH<sub>2</sub>S) ppm; isomer II  $\delta$  1.18, 1.21, 1.36, 1.48, 1.59, 1.65, 1.95, 1.96 (88, each 3H, CH<sub>3</sub>), 2.39, 2.55 (AB system, J<sub>AB</sub> = 14.2 Hz, 2H, CH<sub>2</sub>S) ppm; <sup>13</sup>C-NMR (100.62 MHz, CDCl<sub>3</sub>)  $\delta$  22.81, 25.19, 25.60, 27.05, 28.50, 29.01 (6q, CH<sub>3</sub>), 28.28 (q, C(CH<sub>3</sub>)<sub>2</sub>), 38.76, 40.87, 55.80 (3s,

C(CH<sub>3</sub>)<sub>2</sub>), 47.72, 47.97 (2t, CH<sub>2</sub>S), 82.01 (a, C=C=N), 122.04 (s, C=N), 132.64, 134.81 (2s, C=), 189.09 (s, N=C=C) ppm; MS m/e 304 (M<sup>+</sup>, 28%), 236 (M - C<sub>4</sub>H<sub>4</sub>N, 85%), 180 (M - C<sub>4</sub>H<sub>4</sub>N - C<sub>4</sub>H<sub>4</sub>). (Found : C, 70.82; H, 9.45; N, 9.28; S, 10.52, Calc for C<sub>18</sub>H<sub>28</sub>N<sub>2</sub>S: C, 71.00; H, 9.27; N, 9.20; S, 10.53%)

(b) Photochemical generation of IBN radioals. In a Pyrex Schlenk tube 2.0 g (12 mmol) 13, 229 ml beazons and 6.0 g (36 mmol) AIBN were irradiated with a Hg high-pressure lamp (Hanovia, 450 W) using a Vycor filter. Evolution of gas  $(N_2)$ was observed, which consed after 2 h; at that time a new product was detected by VPC, but 13 was still present. To react 13 completely, an additional 20 g (120 mmol) AIBN were added within 12 h. The solvent was evaporated and the reaction product isolated by column chromatography (silica gel, petroleum ether-ether 5: i). Yield: 3.13 (86%) 50, m.p. 83°; identified by spectroscopic comparison.

Thermolysis of 50. In an NMR tube 30 mg (0.1 mmol) 50 in 0.7 ml toluene-d<sub>a</sub> were heated at 100° for 36 h; the only product obtained was 51 in quantitative yield.

Photolysis of azo t-butane in the presence of 13. In a Pyrex Schlenk tube 504 mg (3 mmol) 13, 15 ml benzene and 852 mg (6 mmol) azo t-butane were irradiated with a Hg high-pressure lamp (Hanovia, 450 W), using a Vycor filter for 6 h. The solvent was evaporated and the products separated by column chromatography (silica gel, petroleum ether-CH<sub>2</sub>Cl<sub>2</sub> 5:1); three fractions were obtained : fraction 1, 112 mg (14%) **46a** or **b**; fraction 2, 214 mg (31%) **39**; fraction 3, 156 mg (30%) 13 (recovered starting material).

Spectroscopic data of 46a or b. <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  1.16, 1.22 (2s, each 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.31, 1.35, 1.37, 1.40 (4s, each 3H, CH<sub>3</sub>), 2.31, 3.04 (AB system, J<sub>AB</sub> = 14.4 Hz, 2H, CH<sub>2</sub>S), 2.85 (s, 1H, CHS), 5.41 (s, 1H, =>CH) ppm; <sup>13</sup>C-NMR (100.62 MHz, CDCl<sub>3</sub>)  $\delta$  27.77, 29.08, 31.18, 36.59 (4q, CH<sub>3</sub>), 30.87, 33.73 (2q, C(CH<sub>3</sub>)<sub>3</sub>), 37.59, 39.17, 41.61, 44.23 (4s, Cq), 47.38 (t, CH<sub>2</sub>S), 62.24 (d, CHS), 140.26 (d, =>CH), 149.59 (s, C=) ppm; MS *m/e* 170 (M - 2 × C<sub>4</sub>H<sub>8</sub>, 49%).

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