115. Synthesis and Chemical Transformations of 4,5-Homosnoutene Derivatives: An Attempted New Access onto the $(CH)_{12}$ Energy Hypersurface

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Pentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{7,9}]dodeca-5,11-diene (**4**) is proposed as a new potential precursor of the truncated tetrahedrane **1**. The synthesis of several new pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene (4,5-homosnoutene) derivatives including homosnouten-5-one (**10**), 5-methylidenehomosnoutene (**19a**) as well as homosnoutene-5-carbaldehyde (**17b**) and their reactions directed toward ring enlargement to the skeleton of **4** are reported. Although all the homosnoutenes resisted ring expansions, several unexpected new polycyclic systems were obtained. Any intermediate developing a cationic center at C(5) of the skeleton of **10** rearranged with release of strain and opening of one or both three-membered rings to give compounds such as **22** and **23**. The aminomethyl derivatives **13a** and **13b**, upon diazotation, underwent a remarkable fragmentation to give **10** and homosnouten-5-ol (**20**), respectively. The 5-(dibromomethyl)homosnouten-5-ol (**14**), upon treatment with *t*-BuLi, rearranged to the pentacyclic ether **15**, while the carbene **11b**, generated by the thermal or photochemical decomposition of the tosylhydrazone salt of **17c**, solely gave **19a** by C,H insertion. The 1,1-dicyclopropylethene unit in **19c** was excited selectively upon irradiation, but the products **26** and **27** of this photochemical rearrangement were derived only from π-participation in diradical intermediates **25a**–**25c**.

Introduction. – Members within families of $(CH)_n$ hydrocarbons are particularly prone to multiple rearrangements [1]. Many of these remarkable thermal and photochemical transformations within the $(CH)_6$, $(CH)_8$, and $(CH)_{10}$ families have been studied and have lead to an understanding and a capability for the prediction of their reaction pathways. This in turn has contributed to determining the limits of orbital-symmetry control in pericyclic reactions.

Although a number of $(CH)_{12}$ hydrocarbons have been synthesized in the meantime [2], the more interesting ones like the most symmetrical truncated tetrahedrane **1** [3], as well as the triene **2** [4] and the tetraene **3** [5], still remain unknown. In recent years, only a few methods have been reported which promised a new entry into the $(CH)_{12}$ family [6]. Hence, there is still an interest in effective syntheses of new $(CH)_{12}$ compounds, especially **1**–**3**.

In our attempt to access the $(CH)_{12}$ energy surface, we focussed our attention on the pentacyclic diene **4** as a potential precursor to **1** and its probable next relatives **2** and/or **3** (see *Scheme 1*).

The concept was born from the observation that upon heating, the $(CH)_{10}$ hydrocarbon snoutene (**7**) undergoes a degenerate rearrangement which can be classified as a symmetry-allowed intramolecular $[_\pi 2_s + _\sigma 2_a + _\sigma 2_a]$ cycloaddition *(Scheme 1)* [7]. By analogy, a photochemically induced intramolecular $[_\pi 2_a + _\sigma 2_a + _\pi 2_a + _\sigma 2_a]$ cycloaddition in the

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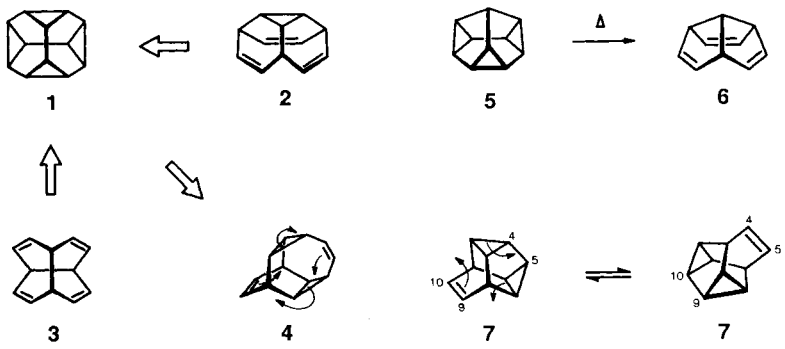
Scheme 1



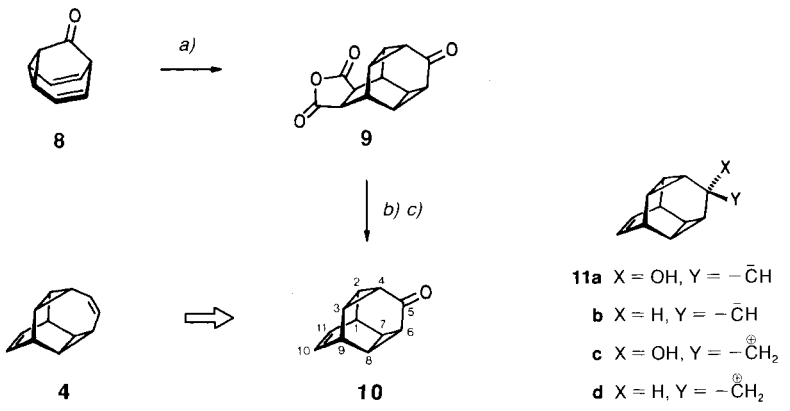
pentacylic diene **4** could lead to the truncated tetrahedrane **1**. Much like diademane (**5**) [8], formed upon irradiation of **7**, and other *cis*-tris-σ-homobenzenes [8] [9], **1** might undergo a thermal rearrangement opening three cyclopropane rings to give **2**. The hydrocarbon **3** had previously been proposed by *Woodward* and *Hoffmann* [10] as a precursor for **1**. Although **3** could not arise from **1** thermally in a concerted $[_\sigma 2_a + _\sigma 2_a + _\sigma 2_a + _\sigma 2_a]$ process, as that would violate orbital-symmetry conservation rules, it could still be formed *via* diradical intermediates.

The relative energies of **1**–**3** have been calculated by *Schulman et al.* [11] using *ab initio* SCF and MM2 methods. Although they estimated E_a for the rearrangement **1**→**2** to be lower than that of a comparable rearrangement, *e.g.* **5**→**6**, they argue strongly for a possible observability of **1**. According to these calculations, the rearrangement of the truncated tetrahedrane to the tricyclic tetraene **3** would be highly endothermic and thereby unlikely.

Synthesis of Pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-en-5-one (= Homosnouten-5-one; 10) and Some of Its Derivatives Including 5-Methylidenehomosnoutene (19a). – Unfortunately dihydrobullvalene derivatives undergo $[_\pi 2 + _\pi 2 + _\pi 2]$ cycloaddition only with extremely reactive dienophiles such as ethylene tetracarbonitrile to give pentacylic systems with the skeleton of pentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{7,9}]dodeca-5,11-diene (**4**) [12] [13]. Since the complete functional-group interconversion of the tetracyano-substituted polycycle into the unsubstituted **4** proved difficult [13], the most straightforward approach appeared to be a ring expansion between C(4) and C(6) of a pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene derivative, because the skeleton of the latter can be constructed by a [2+2+2] cycloaddition of barbaralane and maleic anhydride [8] [9c]. The adduct can be oxidatively decarboxylated to homosnoutene. By analogy, barbaralone (**8**) [14] cycloadds maleic anhydride to give **9** with yields up to 60% [15]. The latter can be converted to homosnouten-5-one (**10**) in moderate yield (42%) by hydrolysis to the coresponding dicarboxylic acid followed by an oxidative decarboxylation with lead tetraacetate in pyridin. In this way, **10** was available in quantities up to 10 g.

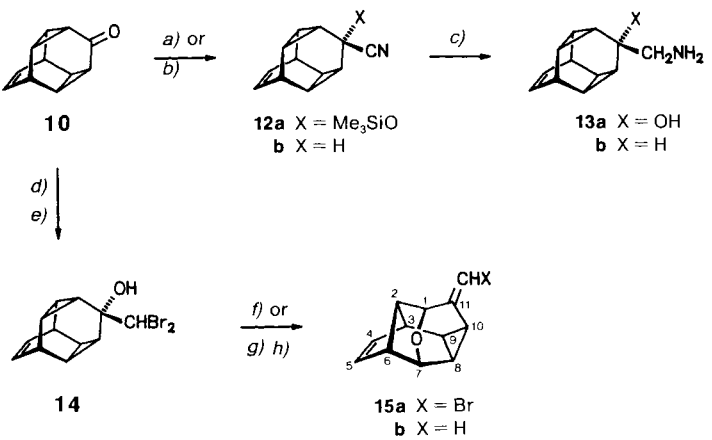
Since ring expansions usually can best be achieved *via* carbocations or carbenes, routes from **10** to precursors of either one of the intermediates **11a–d** *(Scheme 2)*, were developed. Addition of trimethylsilyl cyanide (Me_3SiCN) to **10** catalyzed by ZnI_2 [16] yielded the sensitive cyanohydrin **12a** almost quantitatively which was reduced with $LiAlH_4$ to amino alcohol **13a** (98%; *Scheme 3*). The synthesis of amine **13b** succeeded by

Scheme 2



a) Maleic anhydride, xylene, 160°, 2.5 d. *b*) 1.8M KOH, 10 min, 2N HCl. *c*) $Pb(OAc)_4$, pyridin, 55°, 3 h.

Scheme 3



a) Me_3SiCN, toluene, ZnI_2, reflux, 1 h. *b*) 4-Toluenesulfonyl-methyl isocyanide ($TsCH_2NC$), *t*-BuOK, dimethoxyethane, EtOH. *c*) $LiAlH_4$, Et_2O, reflux, 1 h. *d*) $LiCHBr_2$, THF, −95°. *e*) H^+, −95° to r.t. *f*) SiO_2, chromatography. *g*) *t*-BuLi, THF, −78°. *h*) H^+, −78° to r.t.

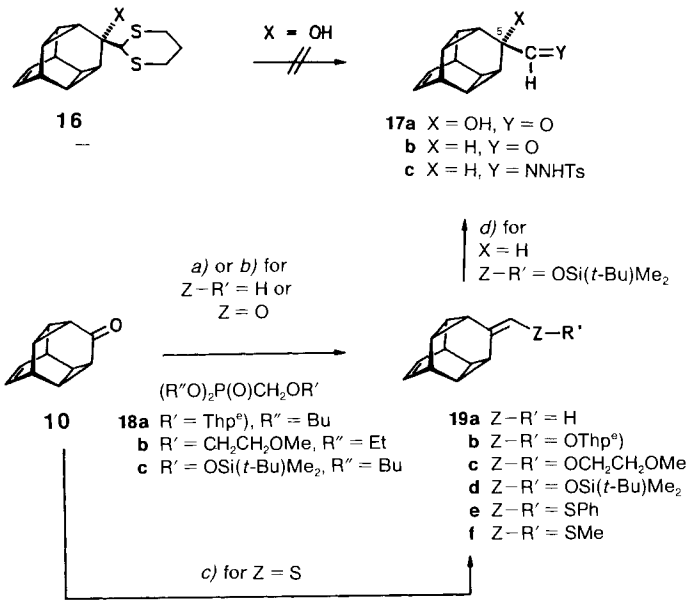
converting **10** into nitrile **12b** (92%) with a method developed by *van Leusen* and coworkers [17] and subsequent reduction with $LiAlH_4$ (95%).

For the intended ring-expansion reaction *via* (dibromomethyl)-substituted alcohols [18], **14** was synthesized by the addition of (dibromomethyl)lithium to **10**. However, **14** underwent an unexpected rearrangement when subjected to column chromatography. The major component was separated from the mixture of new compounds by GLC and identified as 11-(bromomethylidene)-12-oxapentacyclo[5.4.1.$0^{2,6}$.$0^{3,9}$.$0^{8,10}$]dodec-4-ene (**15a**) on the basis of its spectral properties.

The molecular-ion peak in the MS of **15a** at *m/z* 252, 250 indicated that HBr had been eliminated from **14**, and a molecular formula $C_{12}H_{11}BrO$ was proven by high resolution MS. The ^{1}H-NMR spectrum (see *Exper. Part*) with 10 signals in the approximate intensity ratio of 1:1:1:1:1:1:1:1:1:2 revealed the lack of any higher symmetry. Due to the almost complete separation of all signals, it was possible to assign the structure **15a** by selective decoupling experiments. This was confirmed by the ^{13}C-NMR spectrum which also proved the presence of the quarternary C(11).

In an attempt to prepare the tosylhydrazones of the aldehydes **17a** and **17b**, it became apparent that an OH group at C(5) in α-position to two cyclopropane rings caused a distinct tendency towards skeletal rearrangement. *E.g.*, the adduct **16** of lithiodithiane to **10** could not be hydrolyzed to **17a** without rearrangements occurring *(Scheme 4)*. In all attempts, complex mixtures were obtained for which no efforts towards separation were made.

Scheme 4



a) $Me(Ph)_3PBr$, $NaNH_2$, THF, r.t., 24 h. *b*) phosphonate **18**, LDA, THF, −78°, 2 h; refl., 2 h. *c*) $R'SCH_2SiMe_3$, BuLi, −78°, 30 min. *d*) **17b**: Bu_4NF, THF, r.t., 3 h; **17c**: Bu_4NF, NH_2NHTs, THF, r.t., 3 h. *e*) Thp = tetrahydro-2*H*-pyran-2-yl.

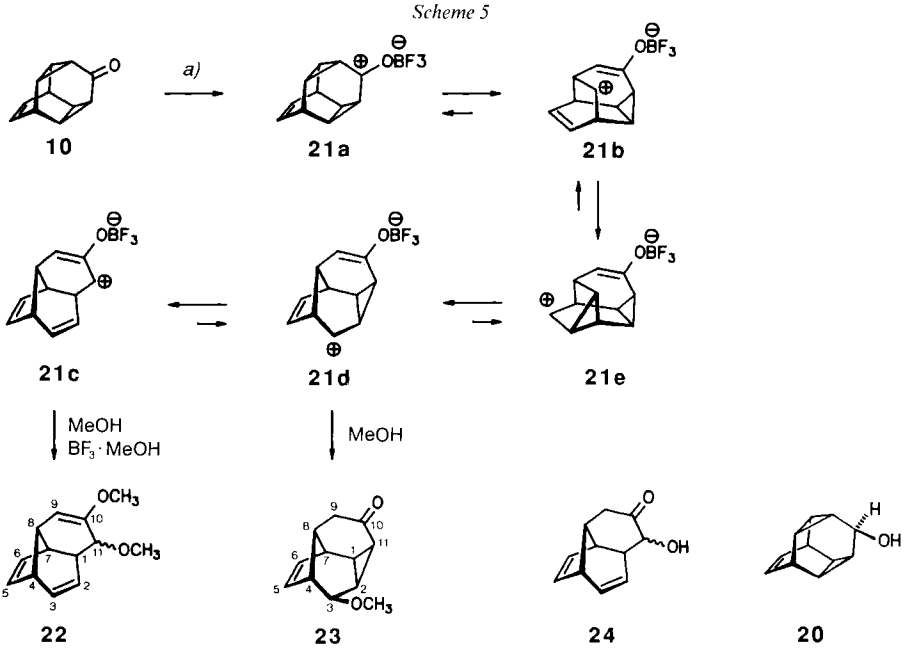
Enol ethers and thioenol ethers **19b–f** appeared to be more suitable for a mild hydrolysis to aldehyde **17b** without an α-OH group. Such enol ethers **19b–d** with common protective groups were obtained in moderate yields by *Wittig-Horner* olefination of **10** with the phosphonates **18** [19]. A *Peterson* olefination utilizing lithiated phenyl or methyl (trimethylsilyl)methyl sulfide [20] led to high yields of the thioenol ethers **19e, f**. Solid **19e** sublimed under reduced pressure, while the liquid **19f** could not be crystallized and had to be purified by short-path distillation. Solely the silyl enol ether **19d** could be converted to aldehyde **17b** without rearrangement by F-induced hydrolysis [21]. Problems in the isolation of **17b** could be overcome by adding a slight excess of tosylhydrazine

to the reaction mixture. The readily obtained tosylhydrazone **17c** was much less labile and could be purified by column chromatography (23–33% from **10**). Although not completely pure, **17c** was suitable for subsequent transformations.

Finally, the unsubstituted 5-methylidenepentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene (= 5-methylidenehomosnoutene; **19a**) was obtained from **10** by *Wittig* olefination [22] (80%) as a volatile white solid which was purified by sublimation.

Attempted Ring Expansions of Homosnoutene Derivatives. – One of the most common ring expansions for ketones is the homologisation with diazomethane [23]. However, **10** was not affected by diazomethane, but in the presence of a molar amount of $BF_3 \cdot Et_2O$ in MeOH, two new products were formed within a few min (ratio *ca.* 1:2) besides traces of by-products. The two main products were separated by GLC or more conveniently by column chromatography. Their spectral properties were consistent with the constitutions of 10,11-dimethoxytricyclo[5.4.0.0^{4,8}]undeca-2,5,9-triene (**22**) and *'endo'*-3-methoxytetracyclo[5.4.0.0^{2,11}.0^{4,8}]undec-5-en-10-one (**23**; see *Scheme 5*).

Scheme 5



a) Et_2O/MeOH 10:1, BF_3, r.t., 20 min.

In the MS, the more volatile component **22** showed M^+ at *m/z* 204, consistent with a molecular formula $C_{13}H_{16}O_2$. No IR absorption characteristic for a carbonyl group was found. In the ^{1}H-NMR spectrum, 2 MeO groups appeared at 3.21 and 3.35 ppm (see *Exper. Part*). The signal of the quarternary C(10) was found in the ^{13}C-NMR spectrum at 156.47 ppm which is in accordance with a vinyl ether. The *d* at 4.53 ppm was assigned to H–C(9). In addition, H–C(11) was found as a *d* at 3.62 ppm. Two further pairs of olefinic signals at 5.24, 5.93, 6.51, and 5.74 ppm were assigned to H–C(2), H–C(3), H–C(5), and H–C(6). The four protons on the bridgeheads C(1), C(4), C(7), and C(8) were found at 2.34, 2.30, 3.02, and 2.80 ppm. The MS of the less volatile **23** showed M^+ at *m/z* 190 and the IR spectrum an absorption at 1685 cm^{-1} characteristic for a ketone. The presence of a three-membered ring was indicated by the high-field shift of H–C(1), H–C(2), and H–C(11) at 1.36, 1.14, and 1.74

ppm, and this was confirmed by the ^{13}C-NMR spectrum with absorptions at 13.78, 26.72, and 31.14 ppm for C(1), C(2), and C(11). The configuration at C(3) was revealed by the coupling constants between H–C(2)/H–C(3) (6.8 Hz) and H–C(3)/H–C(4) (1.2 Hz) which are only consistent with the *'endo'*-position of MeO–C(3).

When stirred in CF_3COOH at r.t., **10** did not rearrange, but the acyloin **24** was obtained in almost 75% yield when the reaction mixture was refluxed for 1 h. The ring expansion of methylidene-cycloalkenes with 4-nitrobenzenesulfonyl azide, successfully applied by *Fitjer* [24] on sensitive small-ring systems with α-cyclopropyl groups, did not work on 5-methylidenehomosnoutene (**19a**). Since **19a** did not react with the azide at room temperature, the mixture was heated in a sealed tube to 100° for several h. In no case could any low-molecular-weight components be obtained from the tarry product mixtures.

In an attempt to subject the amines **13** to a *Demyanov* rearrangement, a remarkable fragmentation was observed. Upon diazotation of **13a** with either $NaNO_2$ in AcOH or isopentyl nitrite in toluene, only homosnoutenone **10** was obtained rather than products derived by rearrangement or elimination. Correspondingly, the diazotization of **13b** with isopentyl nitrite yielded alcohol **20**, as revealed by its ^{1}H-NMR spectrum indicating an intact homosnoutene skeleton (H–C(5) at 4.52 ppm) and by a strong absorption at 3220 cm^{-1} in its IR spectrum.

Following the general method of *Nozaki et al.* [18], the (dibromomethyl)-substituted alcohol **14** was treated with BuLi at low temperature; but rather than giving the ring-enlarged product, an inseparable multitude of components was produced. With the less nucleophilic *t*-BuLi, only one major product was formed which was isolated by GLC. Although the M^+ peak in the MS was the expected *m/z* 172, the ^{1}H-NMR spectrum very much resembled that of **15a**. Spin decoupling of individual resonances allowed complete assignment of the signals to those of the pentacyclic ether **15b** (see *Exper. Part* and *Scheme 3*).

Eventually, the dry sodium salt of the tosylhydrazone **17c** was pyrolyzed in a preheated 'Kugelrohr' apparatus with a temperature gradient 100→220°. At 150°, fine white crystals started to condense in the cooled area. The product obtained (6%) was identified as 5-methylidenehomosnoutene (**19a**) by comparison with authentic material. Upon photolysis of the sodium salt of **17c** at r.t. or – 25°, the yield of **19a** was increased to 48%. No other $C_{12}H_{12}$ hydrocarbons were detected by GC/MS analysis.

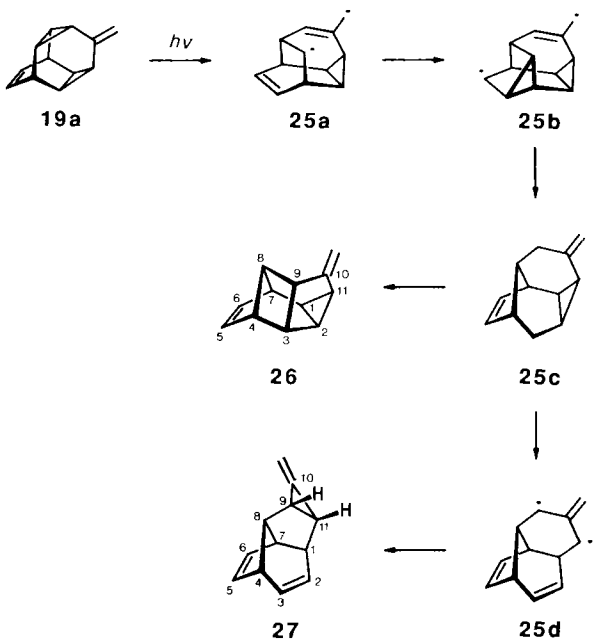
Photochemical Rearrangement of 5-Methylidenehomosnoutene (19a). – In contrast to homosnoutene [8], **19a** contains a 1,1-dicyclo-propylethene subunit. The conjugation between the two cyclopropyl groups and the methylidene double bond raises the energy of its HOMO substantially [25] and, consequently should shift the π–π^* absorption bathochromically by *ca.* 30 nm [26]. Indeed, the longest wavelength absorption is found at 217 nm (ε_{max} = 16000) which means that **19a** has a lower excitation energy than, *e.g.*, butadiene (λ_{max} 209 nm). Therefore, the photochemistry of **19a** with its 1,1-dicyclopropylethene subunit like that of the yet unknown **4** with a 1,2-dicyclopropylethene subunit should differ from that of homosnoutene in which electronic excitation sets off a $[_\pi 2_s + _\sigma 2_s]$ cycloaddition [8] [9c].

To probe for this, **19a** was photolyzed at – 30° in a 'falling film' reactor[2]) using a medium-pressure mercury lamp in a quarz immersion well (in a conventional photolysis

[2]) From Fa. *Normag, Otto Fritz GmbH*, Hofheim/Taunus, FRG.

device or when irradiating **19a** at r.t., only polymeric material was obtained). After a conversion of 70%, the irradiation was stopped. Except for remaining starting material, only two new products (ratio 2:3) were detected in the solution, isolated with considerable losses by GLC and identified as the sensitive tetracyclic methylidenecyclopropane **27** (2.5%) and the pentacyclic hydrocarbon **26** (5%), by means of their mass and NMR spectra.

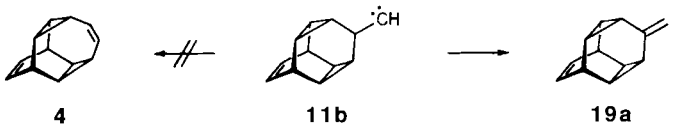
Scheme 6



The ^{1}H-NMR spectrum of **27** showed 6 signals in the olefinic region between 5.5 and 6.5 ppm. Based on their chemical shifts and signal forms these were readily assigned to H–C(2), H–C(3), H–C(5), and H–C(6). Because of overlapping signals, the aliphatic protons could be assigned by a combined interpretation of the ^{13}C-NMR and a COSY spectrum. The signals of the cyclopropane protons appeared as *d* at 1.65 and 2.29 ppm. Very small coupling constants between H–C(8)/H–C(9) and H–C(11)/H–C(1) were interpreted in terms of an *'exo'*-configuration of the methylidenecyclopropane unit for which dihedral angles are close to 90°. The presence of a three-membered ring in **26** was revealed by 3 high-field signals at 1.10, 1.54, and 1.85 ppm, each corresponding to 1H. Two *d* with ^2J = 1.8 Hz at 4.89 and 4.94 ppm were assigned to the methylidene protons. By selective decoupling, a DEPT ^{13}C-NMR, and finally a C,H correlation spectrum, all signals could be assigned except for the distinction between H–C(8) and H–C(9).

Discussion. – Presumably, the main factor which caused most of the attempted ring-expansion reactions to fail is the strain energy which would increase upon ring expanding the homosnoutene skeleton. As tosylhydrazone salts are known to decompose *via* carbene intermediates, and the selectivity of their subsequent reactions generally is low [27], both an α-C–C insertion and an α-C–C insertion were to be expected for the carbene **11b** generated from **17c** *(Scheme 7)*. In spite of that, no C–C-insertion product was found. According to MNDO calculations [28], **19a** is more stable, *i.e.* less strained,

Scheme 7



4 **11b** **19a**

than **4** by 44.5 kJ/mol. Although carbene reactions ought to have an early transition state, the α-C–H insertion wins over the C–C insertion.

Even the homosnoutenone skeleton reveals a high tendency to release strain as soon as a positive charge is developed at C(5). This is yet another example for the manifold thermal and acid-catalyzed rearrangements of $C_{11}H_{10}O$ ketones [29]. *Goldstein* has attributed the ease of isomerization in these so-called longicyclic systems to a special 'bicycloaromaticity' [30].

Obviously, after the attack of a *Lewis* acid at the carbonyl group of **10**, the carbenium ion **21a**, thus, formed would be stabilized by two α-cyclopropyl groups with a perfect bisected conformation (see *Scheme 5*). Cation **21a** is probably opened to the homoallyl cation **21b** which apparently has the correct geometry for homoallylic π-participation of both double bonds. Cation **21d**, formed by another cyclopropylmethyl to homoallyl rearrangement from **21e**, could either be quenched by MeOH to form **23** (49% yield) or be opened at its last cyclopropane ring to give **21c**. Although the methyl enolether **22** (25% yield) could arise from **21c** by methylation with a $BF_3 \cdot$ MeOH complex [31], there is no conclusive rationalization as to why it is formed exclusively rather than the acyloin methyl ether.

In addition to the production of **22** and **23**, the suggested mechanism also accounts for the observation that the CF_3COOH-catalyzed addition of H_2O to **10** yielded the acyloin **24** as the sole product (74.5% yield; see *Scheme 5*). Since this reaction probably proceeds with thermodynamic control, the product **24** must be that derived from the most stable cation. The pentacyclic ethers **15a** and **15b** *(Scheme 3)* are probably formed along a similar route. While the formation of **15a** can be rationalized as an acid-catalyzed removal of the OH group from **14**, rearrangement of the resulting cation, subsequent addition of H_2O and ring closure, no reasonable mechanism for the formation of **15b** can be offered.

The rotational barrier of an α-cyclopropylmethyl radical, which is < 12.5 kJ/mol [32], indicates that a radical is far less stabilized by an α-cyclopropyl substituent than a cation. The fact that **19a** isomerizes upon photochemical initiation *(Scheme 6)*, once more, demonstrates that a cyclopropylmethyl radical is extremely short-lived and rapidly undergoes ring opening. Light absorption by **19a** apparently excites the 1,1-dicyclopropylethene unit to produce the diradical **25a** which rearranges in a process similar to the one observed by *Prinzbach* and coworkers [33] *via* a cascade of homoallyl to cyclopropylmethyl to homoallyl isomerizations. Thus, **26** and **27** eventually result from intramolecular recombination to the rearranged diradicals **25c** and **25d**, respectively.

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Experimental Part

General. Reactions with H_2O- and air-sensitive compounds were carried out under an atmosphere of inert gas. Tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dien-9-one (barbaralone) was synthesized according to [14]; phenyl (trimethylsilyl)methyl sulfide and methyl (trimethylsilyl)methyl sulfide according to [34]; dibutyl {[(2-tetrahydro-2*H*-pyran-2-yl)oxy]methyl}phosphonate, diethyl [(2-methoxyethoxy)methyl]phosphonate, and dibutyl {{[(*tert*-butyl)dimethylsilyl]oxy}methyl}phosphonate according to [19]. Photolysis: Medium-pressure mercury lamp *TQ 150, Hanau Quarzlampengesellschaft.* Capillary GLC: *Siemens Sichromat 3,* N_2 as carrier gas. Prep. GLC: *Varian Aerograph 920, Carlo-Erba FTV 2350;* H_2 as carrier gas. M.p. uncorrected; *Wagner & Münz Schmelzpunktapparat.* IR (cm^{-1}): *Perkin Elmer 297* and *399.* UV: *Perkin-Elmer-Hitachi 200.* ^{1}H-NMR: *Bruker WH270, WM400;* $\delta = 7.26$ for C[D]Cl_3, $\delta = 7.15$ for [D_5]benzene. ^{13}C-NMR: *Bruker WM400.* MS: *Varian MAT CH-7, MAT112* with *Varian Aerograph 1400* (GC/MS), *MAT 311A* (high resolution). Microanalyses: Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Universität Hamburg.

Pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-en-5-one (**10**). A mixture of 2.00 g (15.2 mmol) of barbaralone (**8**), 2.97 g (30.3 mmol) of maleic anhydride, and 20 ml of *o*-dichlorobenzene was heated to 160° for 60 h. The crystals were filtered off and dried: 2.87 g (82%) of *5-oxopentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undecane-10,11-dicarboxylic anhydride* (**9**) which was hydrolyzed with 85 ml (152 mmol) of 10% aq. KOH soln. After addition of dil. HCl soln. (→pH 1), the precipitate was filtered off and dried to yield 2.46 (80%) of *5-oxo-pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undecane-10,11-dicarboxylic acid.* A mixture of 600 mg (2.42 mmol) of the diacid and 6 ml of dry pyridin was flushed with Ar for 30 min, and 2.67 g (6.04 mmol) of $Pb(OAc)_4$ were added. After the evolution of CO_2 had ceased, the mixture was heated for 3 h to 55°, poured into 200 ml of 5% HNO_3 soln., and extracted 5 times with 100 ml of Et_2O. The org. phase was washed twice with 200 ml of 5% HNO_3 soln., twice with 100 ml each of sat. $NaHCO_3$ soln. and brine, and dried ($MgSO_4$). The solvent was removed by distillation over a 50-cm packed column, and finally by short evacuation of the flask. The residue was sublimed twice (70°/0.02 Torr): 149 mg (42%) **10**. IR (KBr): 3050, 2930, 1679, 1655 (C=O), 1383, 1364, 1239, 1082, 936, 691. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.91 (*tm*, $^3J = 6.6$, H–C(4), H–C(6)); 1.99 (*m*, H–C(2), H–C(3), H–C(7), H–C(8)); 3.26 (*m*, H–C(1), H–C(9)); 6.83 (*dd*, $^3J = 4.3, 2.5$, H–C(10), H–C(11)). MS (70 eV): 158 ($M^{+\cdot}$), 129 (100). Anal. calc. for $C_{11}H_{10}O$ (158.2): C 83.51, H 6.37; found: C 83.45, H 6.49.

5-[(Trimethylsilyl)oxy]pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene-5-carbonitrile (**12a**). A mixture of 100 mg (0.63 mmol) of **10**, 1.5 ml of dry toluene, 69 mg (0.70 mmol) of Me_3SiCN, and 5 mg of anh. ZnI_2 was heated to 100° for 1 h. After addition of 30 ml of Et_2O, it was washed with 5 ml of sat. $NaHCO_3$ soln. and brine, and dried ($MgSO_4$). Evaporation of the solvents yielded 164 mg (100%) of crude **12a**. Colorless oil. IR (KBr): 3055, 3030, 2970, 2140 (CN), 1345, 1260 (Si–O), 1250 (sh), 1240, 1207, 1192, 1107 (sh), 110 (sh), 1093 (C–O), 1055, 1030, 992, 942, 920, 875, 855, 818, 782, 770, 760, 742, 728, 687, 662. ^{1}H-NMR (270 MHz, C_6D_6): 0.24 (*s*, Me_3Si); 0.74 (*m*, 2 H), 0.92 (*m*, 2 H; H–C(2), H–C(3), H–C(7), H–C(8)); 1.46 (*tm*, $^3J = 8.2$, H–C(4), H–C(6)); 2.66 (*m*, H–C(1), H–C(9)); 6.42 (*m*, H–C(10), H–C(11)).

5-(Aminomethyl)pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-en-5-ol (**13a**). Dropwise, 159 mg (0.62 mmol) of **12a** in 5 ml of dry Et_2O were added to a suspension of 100 mg (2.64 mmol) of $LiAlH_4$ in 5 ml of Et_2O and refluxed for 1 h. After cooling to r.t., the necessary amount of H_2O was added dropwise (caution!) to hydrolyze all $LiAlH_4$. The liquid was poured off and the residue washed 3 times with 10 ml of Et_2O. The org. phase was dried ($MgSO_4$) and the solvent evaporated: 144 mg (98%) of **13a**. A sample was crystallized from Et_2O. M.p. 113°. IR (KBr): 3350, 3290 (OH, NH_2), 3040, 2995, 2920, 2880, 2835, 1600, 1580, 1435, 1338, 1312, 1135, 1102, 1090, 1040, 1003, 955, 935, 922, 664. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.16 (*m*, H–C(2), H–C(3), H–C(7), H–C(8)); 1.28 (*m*, H–C(4), H–C(6)); 1.77 (br. *s*, NH_2, OH); 2.85, 3.07 (*m*, H–C(1), H–C(9)); 2.92 (*s*, CH_2NH_2); 6.70 (*m*, H–C(10), H–C(11)). MS (70 eV): 172 (2.2, $[M - OH]^+$), 171 (2.7, $[M - H_2O]^+$), 159 (100, $[M - CH_2NH_2]^+$), 141 (27, $[M - CH_2NH_2 - H_2O]^+$). CI-MS: 192 (1.4, $[M + H_2 + H]^+$), 190 (6.6, $[M + H]^+$), 174 (6.8, $[M - H_2O + H_2]^+$), 172 (100, $[M - H_2O]^+$). Anal. calc. for $C_{12}H_{15}NO$ (189.3): C 76.16, H 7.99, N 7.40; found: C 75.46, H 7.58, N 6.83.

Pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene-5-carbonitrile (**12b**). At r.t., 340 mg (3.03 mmol) of sublimed *t*-BuOK were added to a mixture of 200 mg (1.26 mmol) of **10**, 320 mg (1.64 mmol) of $TsCH_2NC$, 4.5 ml of dry dimethoxyethane, and 125 µl of dry EtOH and stirred for 30 min at 40°. After cooling to r.t., the mixture was filtered through 2.5 g of neutral Al_2O_3 (7% H_2O) and the Al_2O_3 washed with 50 ml of Et_2O. Evaporation of the solvent yielded a crude product which was sublimed (60°/0.01 Torr): 196 mg (92%) of **12b**. A sample was crystallized from hexane. M.p. 93°. IR (KBr): 3062, 3050, 3040, 3022, 2975, 2250 (CN), 1347, 1301, 1110, 1098, 980, 970, 960, 923, 782, 732, 695. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.04 (*m*, H–C(2), H–C(3), H–C(7), H–C(8)); 1.49 (*dt*, $^3J_t = 7.8$, $^3J_d = 2.9$, H–C(4), H–C(6)); 2.98, 3.14 (*m*, H–C(1), H–C(9)); 3.53 (*t*, $^3J = 2.9$, H–C(5)); 6.71 (*m*,

H–C(10), H–C(11)). MS (70 eV): 170 (3.9, $[M + 1]^+$), 169 (26, M^+), 168 (100, $[M - H]^+$), 142 (32, $[M - HCN]^+$), 128 (32, $[M - HCN - CH_2]^+$), 115 (62, $[M - HCN - C_2H_5]^+$). Anal. calc. for $C_{12}H_{11}N$ (169.2): C 85.17, H 6.55, N 8.28; found: C 84.74, H 6.64, N 8.45.

Pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene-5-methylamine (**13b**). As described for **13a**, 224 mg (5.90 mmol) of $LiAlH_4$ and 100 mg (0.59 mmol) of **12b** were reacted and worked up. Evaporation of the solvent yielded 97 mg (95%) of **13b** as a viscous oil. From a sample of 20 mg, only 0.5 mg of **13b** recrystallized from hexane. M.p. 93°. IR (film): 3360 (br.), 3280 (br., NH), 3035, 3000, 2920, 2840, 1580, 1555 (sh), 1535, 1470, 1453, 1440, 1419, 1382, 1370, 1337, 1315, 1252, 1228, 1086, 985, 940, 922, 775, 748, 712, 661, 644. ^{1}H-NMR (270 MHz, C_6D_6): 0.70 (*m*, 2 H), 0.86 (*m*, 2 H; H–C(2), H–C(3), H–C(7), H–C(8)); 0.98 (*dt*, $^3J_t = 7.8$, $^3J_d = 2.8$, H–C(4), H–C(6)); 1.16 (br. *s*, NH_2); 2.15 (*tt*, $^3J = 6.2, 2.8$, H–C(5)); 2.72 (*d*, $^3J = 6.2$, CH_2NH_2); 2.77 (*m*, 1 H), 2.88 (*m*, 1 H; H–C(1), H–C(9)); 6.66 (*m*, H–C(10), H–C(11)). MS (70 eV): 173 (1.1, *M*), 172 (2.6, $[M - H]^+$), 141 (21, $[M - C_2H_4]^+$), 68 (100).

Diazotization of **13a**. A mixture of 100 mg (0.53 mmol) of **13a**, 124 mg (1.06 mmol) of isopentyl nitrite, and 5 ml of dry toluene was refluxed under Ar for 4 h. It was poured onto 5 ml of H_2O, extracted 3 times with 10 ml of Et_2O, the extract dried ($MgSO_4$) and evaporated, and the residue (106 mg) purified by CC (10 g SiO_2, Et_2O/pentane 1:4 and 1:2): 12 mg (14%) of **10**, according to GLC, ^{1}H-NMR, and MS identical with an authentic sample.

Diazotization of **13b**. As described for **13a**, 100 mg (0.58 mmol) of **13b** were diazotized and worked up. After evaporation, the residue (121 mg) was purified by CC (15 g of neutral Al_2O_3 (7% H_2O), Et_2O/pentane 10:1, 4:1, and 1:1, Et_2O): 13 mg (14%) of *pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-en-5-ol* (**20**). White crystals. M.p. 90°. IR (KBr): 3220 (br., OH), 3130 (br.), 3030, 3000, 2980, 2930, 2860, 2840 (sh), 2870 (sh), 1419, 1356, 1338, 1297, 1279, 1250, 1222, 1087, 1078, 1063, 1032, 1019 (C–O), 951, 935, 925, 907, 708, 663, 655, 650. ^{1}H-NMR (270 MHz, C_6D_6): 0.76 (*m*, 2 H), 0.93 (*m*, 2 H; H–C(2), H–C(3), H–C(7), H–C(8)); 1.24 (*dm*, $^3J = 3.9$, H–C(4), H–C(6), OH); 2.61 (*m*, 1 H), 2.74 (*m*, 1 H; H–C(1), H–C(9)); 4.52 (*t*, $^3J = 3.9$, H–C(5)); 6.60 (*m*, H–C(10), H–C(11)). MS (70 eV): 161 (1.3, $[M + 1]^+$), 160 (10, M^+), 159 (10, $[M - H]^+$), 143 (10, $[M - OH]^+$), 142 (33, $[M - H_2O]^+$), 141 (37, $[M - H_2O - H]^+$), 91 (100).

5-(Dibromomethyl)pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-en-5-ol (**14**). At 100°, 242 mg (1.39 mmol) of dibromomethane in 2 ml of dry THF were added dropwise to 1.39 mmol of lithium diisopropylamide (LDA) in 10 ml of dry THF and stirred for 1 h. To this soln., 200 mg (1.26 mmol) of **10** in 10 ml of THF were added dropwise, and the mixture was stirred for 1 h. Then it was hydrolyzed with 10 ml of sat. NH_4Cl soln. and warmed slowly to r.t. After addition of 50 ml of Et_2O the aq. phase was extracted 3 times with 10 ml of Et_2O each, and the org. phase was washed with 10 ml of 20% citric acid, 20 ml of H_2O, 10 ml of sat. $NaHCO_3$, and brine. Drying and evaporation yielded 449 mg (100%) of **14** as a viscous oil. IR (film): 3420 (OH). ^{1}H-NMR (270 MHz, $CDCl_3$): 1.19 (*m*, H–C(2), H–C(3), H–C(7), H–C(8)); 1.55 (*t*, H–C(4), H–C(6)); 2.54 (br. *s*, OH); 2.91 (*m*, 1 H), 3.03 (*m*, 1 H, H–C(1), H–C(9)); 5.94 (*s*, $CHBr_2$); 6.69 (*m*, H–C(10), H–C(11)). MS (70 eV): 316, 314, 312 (5.5, 11, 5.5, $[M - H_2O]^+$), 253, 251 (28, 28, $[M - Br]^+$), 252, 250 (17, 17, $[M - HBr]^+$), 172 (100, $[M - 2Br]^+$), 154 (50, $[M - 2Br - H_2O]^+$).

11-(Bromomethylidene)-12-oxapentacyclo[5.4.1.0^{2,6}.0^{3,9}.0^{8,10}]dodec-4-ene (**15a**). On CC (15 g SiO_2, AcOEt, AcOEt/MeOH 1:1) of 200 mg (0.60 mmol) of **14**, a mixture of products (186 mg) was obtained. Separation by GLC (1 m 10% *SE 54*, 180°) yielded 5 mg (3.3%) of **15a** as a viscous oil. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.61 (*m*, *AB* of *ABX*, $^3J(8,10) = 7.9$, $^3J(9,10) = 7.9$, H–C(8), H–C(9)); 2.18 (*ddd*, $^3J = 7.9, 7.9, 2.0$, $^4J = 1.0$, H–C(10)); 2.53 (*ddd*, $^3J = 6.1, 2.5, 1.4$, H–C(3)); 2.79 (*ddd*, $^3J = 6.2, 4.0, 3.0$, H–C(6)); 3.15 (*ddd*, $^3J = 6.9, 6.2, 6.1$, H–C(2)); 4.31 (*ddd*, $^3J = 6.2$, 4.0, $^4J = 1.1$, H–C(7)); 4.37 (*dd*, $^3J = 6.9$, 2.0, H–C(1)); 5.72 (*dd*, $^3J = 5.9$, 3.0, H–C(5)); 6.10 (*s*, =CHBr); 6.18 (*dd*, $^3J = 5.9$, $= 2.5$, H–C(4)). ^{13}C-NMR (100.62 MHz, $CDCl_3$, JMODUL): 19.04, 25.00, 38.23 (+, C(8), C(9), C(10)); 52.66 (probably 2 signals), 53.28 (+; C(2), C(3), C(6)); 70.09, 76.56 (+, C(1), C(7)); 97.93 (+, =CHBr); 126.68, 140.03 (+, C(4), C(5)); 140.78 (–, C(11)). MS (70 eV): 252, 250 (M^+), 223, 221 ($[M - CO]^+$), 222, 220 ($[M - HCO]^+$), 171 (100, $[M - Br]^+$).

11-Methylidene-12-oxapentacyclo[5.4.1.0^{2,6}.0^{3,9}.0^{8,10}]dodec-4-ene (**15b**). A 15% soln. of *t*-BuLi in hexane (170 µl, 0.4 mmol) was added to 61 mg (0.18 mmol) of **14** in dry THF (2 ml) at –78° and stirred for 30 min. The mixture was hydrolyzed with 5 ml of sat. NH_4Cl soln. and warmed slowly to r.t. It was extracted 3 times with 10 ml of Et_2O, the extract dried ($MgSO_4$) and evaporated, and the residue (30 mg) purified by GLC (1 m 10% *SE 54*, 150°): 1 mg (3%) of **15b**. ^{1}H-NMR (270 MHz, C_6D_6): 0.99 (*m*, $^3J \approx 8.0, 8.0$, $^4J \approx 1.5$, $^3J \approx 1.0$, H–C(9)); 1.12 (*ddd*, $^3J \approx 8.0$, $^3J = 7.6$, 6.2, H–C(8)); 1.54 (*ddd*, $^3J \approx 8.0$, $^3J = 7.6$, $^4J = 1.5$, H–C(10)); 2.21 (*ddd*, $^3J = 6.1$, 2.5, $^3J \approx 1.0$, H–C(3)); 2.62 (*ddd*, $^3J = 6.7$, 3.3, 2.9, H–C(6)); 2.85 (*ddd*, $^3J = 6.9$, 6.7, 6.1, H–C(2)); 4.09 (*ddd*, $^3J = 6.2$, 3.3, $^4J \approx 1.5$, H–C(7)); 4.22 (*dd*, $^3J = 6.9$, $^4J = 1.5$, H–C(1)); 4.78 (*d*, $^2J = 1.4$), 4.81 (*d*, $^2J = 1.4$), (=CH_2); 5.42 (*dd*, $^3J = 5.7$, 2.9, H–C(5)); 5.85 (*dd*, $^3J = 5.7$, 2.5, H–C(4)). MS (70 eV): 173 (9.8, $[M + 1]^+$), 172 (68, M^+), 171 (16, $[M - H]^+$), 157 (12, $[M - CH_3]^+$), 143 (54, $[M - CH_2CH_3]^+$), 128 (100).

5-(1,3-Dithian-2-yl)pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-en-9-ol (**16**). At –78°, 1.32 ml (1.52 mmol) of 1.15M BuLi in hexane were added dropwise to 152 mg (1.26 mmol) of 1,3-dithiane in 10 ml of dry *THF* and stirred

for 1 h at −78° and 2 h at 0°. Then, 200 mg (1.26 mmol) of **10** in 10 ml of dry THF were added at −78° and stirred for 1 h. The mixture was quenched with 140 µl of AcOH and warmed to r.t. Addition of 70 ml of Et_2O, filtration through 1.5 g of neutral Al_2O_3 (7% H_2O), and evaporation yielded 341 mg (97%) of **16** which was crystallized from hexane. M.p. 116°. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.09 (*m*, 2 H); 1.25 (*m*, 2 H, H–C(2), H–C(3), H–C(7), H–C(8)); 1.53 (*tm*, ^3J = 8.0, H–C(4), H–C(6)); 1.90 (*m*, 1 H); 2.09 (*m*, 1 H, $SCH_2CH_2CH_2S$); 2.25 (br. *s*, OH); 2.92 (*m*, $SCH_2CH_2CH_2S$); 2.98 (*m*, H–C(1), H–C(9)); 4.47 (*s*, $SCHS$); 6.71 (*m*, H–C(10), H–C(11)). IR (KBr): 3490 (OH), 3040, 2990, 2930, 2890, 2575, 1420, 1375, 1338, 1303, 1275, 1192, 1123, 1075, 1020, 985, 945, 930, 901, 836, 780, 768, 715, 683, 672. MS (70 eV): 278 (7.5, $M^{+\cdot}$), 261 (2.3, $[M - OH]^+$), 260 (9.5, $[M - H_2O]^{+\cdot}$), 159 (100). Anal. calc. for $C_{15}H_{16}OS_2$ (278.4): C 64.71, H 6.52, S 23.03; found: C 64.60, H 6.45, S 23.12.

*5-{[(Tetrahydro-2*H*-pyran-2-yl)oxy]methylidene}pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene* (**19b**). At −78° 292 mg (0.95 mmol) of dibutyl{[(tetrahydro-2*H*-pyran-2-yl)oxy]methyl}phosphonate were added to 0.95 mmol of LDA in 5 ml of dry THF *via* syringe and stirred for 2 h. To the mixture, 100 mg (0.63 mmol) of **10** in 5 ml of dry THF were added and stirred for 2 h, warmed to r.t., and refluxed for 1 h. After cooling to r.t., 10 ml of Et_2O were added, and the mixture was washed twice with 5 ml of 20% citric acid, 5 ml of H_2O, twice with 5 ml of sat. $NaHCO_3$ soln., and 5 ml of brine. Drying ($MgSO_4$) and evaporation yielded a crude product which was crystallized form hexane/*t*-BuOMe 2:1: 86 mg (53%) **19b**. White crystals. M.p. 92–93°. IR (KBr): 3020, 3000, 2990, 2940, 2910, 2855, 2840, 1567, 1455, 1440, 1432, 1413, 1352, 1341 (sh), 1335 (sh), 1313, 1309, 1220, 1190, 1179, 1145 (sh), 1139 (C–O), 1125 (C–O), 1112 (C–O), 1099, 1975, 1065 (sh), 1035, 1009, 965, 937, 923, 897, 880, 861, 811, 800, 783, 717, 663. ^{1}H-NMR (270 MHz, C_6D_6): 0.98 (*m*, 2 H), 1.12 (*m*, 2 H, H–C(2), H–C(3), H–C(7), H–C(8)); 1.57 (*dt*, ^3J_t = 7.5, ^4J_d = 1.8, 1 H), 2.54 (*dt*, ^3J_t = 7.5, ^4J_d = 1.8, 1 H, H–C(4), H–C(6)); 1.17–1.84 (*m*, $CCH_2CH_2CH_2C$); 2.94 (*m*, H–C(1), H–C(9)); 3.44 (*dm*, ^2J = 11.0, 1 H), 3.89 (*dm*, ^2J = 11.0, ^3J = 3.0, 1 H; OCH_2C); 4.91 (*dd*, ^3J = 3.4, 2.6, O_2CHCH_2); 6.57 (*dd*, ^3J = 4.2, 2.6, H–C(10), H–C(11)); 6.60 (*s*, C=CHO). MS (70 eV): 256 (2.9, $M^{+\cdot}$), 172 (32, $[M - Thp]^+$), 144 (11, $[M - Thp - CO]^{+\cdot}$), 85 (100, Thp).

5-[(2-Methoxyethoxy)methylidene]pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene (**19c**). Analogously to **19b**, 1.39 mmol of LDA, 314 mg (1.39 mmol) of diethyl [(2-methoxyethoxy)methyl]phosphonate, and 200 mg (1.26 mmol of **10** were reacted and worked up to yield a crude product which was purified by CC (10 g of neutral Al_2O_3 (7% H_2O), Et_2O/pentane 1:4): 194 mg (67%) of **19c**. Viscous oil. IR (film): 3035, 3001, 2930, 2860, 2805, 1675, 1465, 1418, 1387, 1359, 1349, 1338, 1228, 1196, 1155 (C–O), 1137 (C–O), 1110 (C–O), 1085, 1029, 1013, 942, 935, 918, 801, 972, 781, 662. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.12 (*m*, 2 H), 1.22 (*m*, 2 H; H–C(2), H–C(3), H–C(7), H–C(8)); 1.66 (*dt*, ^3J_t = 7.4, ^4J_d = 1.9, 1 H), 2.26 (*dt*, ^3J_t = 7.6, ^4J_d = 1.9, 1 H; H–C(4), H–C(6)); 3.09 (*m*, H–C(1), H–C(9)); 3.42 (*s*, MeO); 3.63 (*m*, 5 lines, *ca.* 2:1:2:1:2, $MeOCH_2$); 3.89 (*m*, 5 lines, *ca.* 2:1:2:1:2, $CH_2OCH{=}C$); 6.18 (*s*, C=CHO); 6.68 (*dd*, ^3J = 4.4, 2.5, H–C(10), H–C(11)). MS (70 eV): 230 (14, $M^{+\cdot}$), 154 (36, $[M - HOCH_2CH_2OMe]$), 59 (100, $[CH_3{-}C(OH)CH_3]^+$).

5-{{[(tert-Butyl)dimethylsilyl]oxy}methylidene}pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene (**19d**). Analogously to **19b**, 3.79 mmol of LDA, 1.29 g (3.79 mmol) of dibutyl {{[(*tert*-butyl)dimethylsilyl]oxy}methyl}phosphonate and 400 mg (2.53 mmol) of **10** were reacted and worked up to yield a crystalline product which was sublimed twice (60°/0.02 Torr): 369 mg (51%) of **19d**. M.p. 84°. At r.t., it decomposed slowly, therefore, it had to be stored at −30°. IR (KBr): 3075, 3035, 3010, 2960, 2945, 2905, 2870, 1685, 1485, 1429, 1399, 1367, 1347, 1263, 1258, 1243, 1200, 1181 (C–O), 1158 (C–O), 1135 (C–O), 957, 945, 913, 875, 843, 838, 815, 785, 713, 680, 580, 567. ^{1}H-NMR (270 MHz, $CDCl_3$): 0.12 (*s*, Me_2Si); 0.89, (*s*, *t*-BuSi); 1.05 (*m*, 2 H), 1.15 (*m*, 2 H; H–C(2), H–C(3), H–C(7), H–C(8)); 1.62 (*dt*, ^3J_t = 7.5, ^4J_d = 1.9, 1 H), 2.17 (*dt*, ^3J_t = 7.5, ^4J_d = 1.9, 1 H, H–C(4), H–C(6)); 3.02 (*m*, H–C(1), H–C(9)); 6,20 (*s*, C=CHO); 6.52 (*dd*, ^3J = 4.1, 1.5; H–C(10), H–C(11)). MS (70 eV): 286 (7.5, $M^{+\cdot}$), 229 (7.6, $[M - (t\text{-Bu})]^+$), 155 (21, $[M - (t\text{-Bu})MeSiO]^{+\cdot}$), 73 (100, $[SiMe_3]^+$). Anal. calc. for $C_{18}H_{26}OSi$ (286.5): C 75.46, H 9.15; found: C 75.05, H 9.24.

5-[(Phenylthio)methylidene]pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene (**19e**). At −78°, 0.48 ml (0.70 mmol) of 1.44M BuLi in hexane was added to 124 mg (0.63 mmol) of phenyl (trimethylsilyl)methyl sulfide in 5 ml of dry THF at −78° and stirred for 30 min at −78° and 2 h at 0°. At −78°, 100 mg (0.63 mmol) of **10** in 5 ml of dry THF were added, and the mixture was stirred for 2 h at −78° and 2 h at r.t. Quenching with 40 µl of AcOH, addition of 30 ml of Et_2O, filtration through 1 g of neutral Al_2O_3 (7% H_2O), and evaporation yielded a crude product which was purified by sublimation (70°/0.01 Torr): 161 mg (96%) of **19e**. M.p. 53° (pentane). IR (KBr): 3045, 3020, 2945, 1607, 1582, 1475, 1438, 1398, 1387, 1341, 1283, 1227, 1203, 1091, 1072, 1033, 1019, 943, 938, 921, 807, 795, 781, 735, 702, 684, 678. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.43 (*m*, H–C(2), H–C(3), H–C(7), H–C(8)); 2.04 (*dt*, ^3J_t = 7.5, ^4J_d = 2.6, 1 H); 2.49 (*dt*, ^3J_t = 7.5, ^4J_d = 2.6, 1 H; H–C(4), H–C(6)); 3.17 (*m*, H–C(1), H–C(9)); 6.03 (*s*, =CH–SPh); 6.73 (*dd*, ^3J = 4.1, 2.4; H–C(10), H–C(11)); 7.14 (*m*, 1 arom. H); 7.32 (*m*, 4 arom. H). MS (70 eV): 266 (1.8, $[M + 2]^+$), 265 (6.5, $[M + 1]^+$), 264 (29, $M^{+\cdot}$), 187 (11, $[M - Ph]^+$), 155 (100 $[M - PhS]^+$). Anal. calc. for $C_{18}H_{16}S$ (264.4). C 81.77, H 6.10, S 12.13; found: C 81.92, H 6.08, S 12.28.

5-[(Methylthio)methylidene]pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene (**19f**). Analogously to **19e**, 252 mg (2.52 mmol) of methyl(trimethylsilyl)methyl sulfide, 1.9 ml (2.78 mmol) of 1.44M BuLi, and 100 mg (0.63 mmol) of **10** were reacted and worked up to yield a crude product which was purified by short-path distillation (80–100°/0.02 Torr): 118 mg (92%) of **19f**. Colourless oil. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.27 (*m*, 2 H); 1.37 (*m*, 2 H, H–C(2), H–C(3), H–C(7), H–C(8)); 1.86 (*dt*, $^3J_t = 6.5$, $^4J_d = 2.2$, 1 H), 2.27 (*dt*, $^3J_t = 6.5$, $^4J_d = 2.2$, 1 H; H–C(4), H–C(6)); 2,27 (*s*, MeS); 3.11 (*m*, H–C(1), H–C(9)); 5.75 (*s*, =C*H*SMe); 6.69 (*dd*, $^3J = 4.3$, 2.6; H–C(10), H–C(11)). IR (film): 3040, 3005, 2940, 2905, 1600, 1580, 1572, 1543, 1428, 1413, 1387, 1380 (sh), 1335, 1309, 1281, 1240, 1222, 1198, 1102, 1084, 1069, 1028, 938, 930 (sh), 919, 842, 832, 802, 794, 783, 759, 665. MS (70 eV): 204 (2.1, $[M + 2]^+$), 203 (5.9, $[M + 1]^+$), 202 (37, M^+), 187 (43, $[M - Me]^+$), 155 (100, $[M - MeS]^+$).

5-Methylidenepentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene (**19a**). A suspension of 1.97 g (50.6 mmol) of $NaNH_2$ and 8.66 g (25.3 mmol) of $Me(Ph)_3PBr$ in 200 ml of dry THF was refluxed for 3 h. After filtration, 2.00 g (12.7 mmol) of **10** in 100 ml of dry THF were added dropwise to the ylid and stirred at r.t. for 24 h. The mixture was poured onto 500 ml of ice and extracted 5 times with 100 ml of pentane each. The org. phase was washed twice with 100 ml of H_2O and dried ($MgSO_2$). The solvent was removed by distillation over a 50-cm packed column and finally by short evacuation to leave a yellow oil which solidified on shaking with 100 ml of pentane. The solid was extracted 5 times with 30 ml of pentane. The pentane was evaporated to yield a white solid which was sublimed at 50°/3 Torr: 1.56 g (79%) of **19a**. White crystals. M.p. 88°. IR (KBr): 3050, 2950, 1612, 1342, 1335, 941, 912, 840, 680, 669. ^{1}H-NMR (270 MHz, C_6D_6): 1.05 (*ddd*, $^3J = 7.6$, 2.6, $^2J = 3.3$, H–C(2), H–C(3), H–C(7), H–C(8)); 1.73 (*t*, $^3J = 7.6$, H–C(4), H–C(6)); 2.88 (*m*, H–C(1), H–C(9)); 5.02 (*s*, $=CH_2$); 6.56 (*dd*, $^3J = 4.4$, 1.8, H–C(10), H–C(11)). MS (70 eV): 156 (M^+), 141 (100). HR-MS: 156.0917 (M^+, calc. 156.0939). Anal. calc. for $C_{12}H_{12}$ (156.2): C 92.26, H 7.74; found: C 90.97, H 7.80.

Pentacyclo[5.4.0.0^{2,4}.0^{3,9}.0^{6,8}]undec-10-ene-5-carboxaldehyde 4-Toluenesulfonylhydrazone (**17c**). At r.t., 850 mg of crude **19d** (obtained from 400 mg (2.53 mmol) of **10**), 518 mg (2.78 mmol) of 4-toluolsulfonylhydrazine, and 4.4 ml (2.78 mmol) of 0.63M Bu_4NF in THF were stirred for 3 h at r.t. After addition of 100 ml of Et_2O, the mixture was washed twice with 10 ml of H_2O and 10 ml of brine, the extract dried ($MgSO_4$) and evaporated, and the residue purified by CC (70 g SiO_2, Et_2O/pentane 1:1): 200 mg (23% based on **10**) of **17c** (95% by TLC) as a colorless viscous oil. A sample was crystallized from hexane. M.p. 50–55°. IR (KBr): 3450 (br., NH), 3210 (NH), 3050, 2960 (sh), 2940, 2870, 1600, 1450, 1355, 1320, 1308, 1190, 1170, 1095, 1065, 1035, 970, 955, 935, 915, 857, 841, 819, 782, 740, 690, 675, 592, 550. ^{1}H-NMR (270 MHz, C_6D_6): 0.56–0.83 (*m*, H–C(2), H–C(3), H–C(7), H–C(8), H–C(4), H–C(6)); 1.28 (br. *s*, NH); 1.82 (*s*, Me); 2.69 (*m*, H–C(1), H–C(9)); 3.04 (*dt*, $^3J_d = 6.4$, $^3J_t = 3.0$), 6.57 (*m*, H–C(10), H–C(11), CH=N); 6.76 (*dm*, $^3J = 8.2$, arom. H); 8.01 (*dm*, $^3J = 8.2$, arom. H). MS (70 eV): 342 (1.2, $[M + 2]^+$), 341 (3.4, $[M + 1]^+$), 340 (1.4, M^+), 185 (8, $[M - SO_2C_7H_7]^+$), 91 (100%).

Pyrolysis of the Sodium Salt of **17c**. At r.t. 251 mg (0.74 mmol) of **17c**, 22 mg (0.74 mmol) of 80% NaH, and 10 ml of dry THF were stirred for 1 h. The solvent was condensed into a trap and the precipitate dried for 48 h *in vacuo* (276 mg). It was not further characterized. Under dry Ar, 146 mg (0.40 mmol) of the sodium salt of **17c** was filled into a dry flask. It was connected with a short-path distillation apparatus, the receiver cooled with dry ice, and the flask evacuated to 0.01 Torr. It was introduced into the 'Kugelrohr' oven (Fa. *Büchi*, Buchs, Switzerland) with an oven temp. of 100°, and the temp. was increased 10°/5 min. At 150°, fine white crystals sublimed into the receiver. After 1 h 20 min, the reaction was stopped and the receiver warmed to r.t.: 8 mg of crude product, 3 major components. GLC (25 m *OV 101*, 140°): t_R 1.49 (rel. amount 20% of **I**), 3.28 (47% of **II**), 7.39 min (29% of **III**). **I**: MS (70 eV): 186 (highest mass peak), 142 (100). **II**: **19a** (6%; yield as calc. from the GLC integral); ^{1}H-NMR and MS identical to that of an authentic sample (*vide supra*). **III**: MS (70 eV): 212 (highest mass peak), 111 (100%).

Photolysis of the Sodium Salt of **17c**. At r.t., 162 mg (0.45 mmol) of **17c**, *ca.* 11 mg (0.45 mmol) of deparaffinized NaH, and 8 ml of dry THF were stirred for 1 h in a dry *Pyrex* tube, filled with Ar, and equipped with a *Pyrex* immersion well and a 150-W mercury lamp. To this suspension, 100 ml of dry THF were added, the mixture was cooled (MeOH/dry ice) to −25° and photolyzed for 1 h, while Ar was bubbled through the suspension. The resulting soln. was diluted with 100 ml of Et_2O, the Et_2O phase washed 3 times with 10 ml of H_2O and 10 ml of brine, dried ($MgSO_4$), and evaporated by distillation through a 50-cm packed column and finally by short evacuation, and the residue (97 mg) sublimed (50°/0.1 Torr): 58 mg (48%) of **19a**, according to GLC, ^{1}H-NMR, and MS identical with an authentic sample.

10,11-Dimethoxytricyclo[5.4.0.0^{4,8}]undeca-2,5,9-triene (**22**) *and 3-Methoxytetracyclo[5.4.0.0^{2,11}.0^{4,8}]undec-5-en-10-one* (**23**). A mixture of 50 mg (0.32 mmol) of **10** and 45 mg (0.32 mmol) of $BF_3 \cdot Et_2O$ was stirred in 5 ml of Et_2O/MeOH 10:1 for 20 min. Then, 10 ml of sat. $NaHCO_3$ soln. were added, and the org. phase was washed with 5 ml of H_2O and brine. Drying ($MgSO_4$) and evaporation yielded a crude product which was separated by CC (15 g SiO_2, Et_2O/pentane 1:4): 16 mg (25%) of **22** (R_f 0.70) and 32 mg (49%) of **23** (R_f 0.13).

22: Colorless oil. IR (film): 3090, 3010, 2930, 2880, 2810, 1649, 1460, 1442, 1382, 1365, 1342, 1220, 1200, 1164, 1089, 1037, 1022, 1010, 977, 950, 908, 883, 847, 818, 780, 742, 729, 690. ^{1}H-NMR (270 MHz, C_6D_6): 2.30 (*m*, ^3J = 6.0, 4.9, 2.9, H–C(4)); 2.34 (*m*, ^3J = 4.3, 2.9, 1.4, H–C(1)); 2.80 (*m*, ^3J = 6.5, 5.6, 4.9, H–C(8)); 3.02 (*m*, ^3J = 6.5, 3.1, 1.4, H–C(7)); 3.21 (*s*, MeO); 3.35 (*s*, MeO); 3.62 (*d*, ^3J = 2.9, H–C(11)); 4.53 (*d*, ^3J = 5.6, H–C(9)); 5.24 (*ddd*, ^3J = 9.4, 4.3, ^4J = 1.4, H–C(2)); 5.74 (*dd*, ^3J = 5.8, 3.1, H–C(6)); 5.93 (*dd*, ^3J = 9.4, 6.0, H–C(3)); 6.51 (*dd*, ^3J = 5.8, 2.9, H–C(5)). ^{13}C-NMR (100.62 MHz, $CDCl_3$; JMODUL): 35.56, 38.77, 42.61, 44.96 (+, C(1), C(4), C(7), C(8)); 54.33 (+, MeO); 57.92 (+, *Me*O–C(10)); 79.38 (+, C(11)); 98.37, (+, C(9)); 126.10, 131.03, 134.99, 144.93 (+, C(2), C(3), C(5), C(6)); 156.47 (–, C(10)). MS (70 eV): 205 (4.8, $[M + 1]^+$), 204 (37, $M^{+\cdot}$), 173 (24, $[M - MeO]^+$), 172 (58, $[M - MeOH]^+$), 157 (38, $[M - Me - MeO]^+$), 141 (28, $[M - 2\,MeOH]^+$), 129 (100).

23: White crystals. M.p. 57°. IR (KBr): 3060, 2995, 2935, 2900, 2850, 2820, 1685 (CO), 1460, 1447, 1435, 1388, 1360, 1349, 1241, 1221, 1184, 1132, 1111, 1082, 1058, 998, 953, 947, 912, 899, 879, 857, 786, 715, 702, 428. ^{1}H-NMR (270 MHz, C_6D_6): 1.14 (*m*, ^3J = 8.1, 8.0, 6.8, 1.0, H–C(2)); 1.36 (*dddd*, ^3J = 8.0, 7.2, 3.2, 1.6, H–C(1)); 1.74 (*dd*, ^3J = 8.1, 7.2, H–C(11)); 1.94 (*m*, ^3J = 8.4, 6.3, 4.6, 0.9, H–C(8)); 2.04 (*m*, ^3J = 6.3, 3.2, 2.8, 1.0, H–C(7)); 2.07 (*dd*, ^2J = 18.9, ^3J = 4.6, *'exo'*-H–C(9)); 2.45 (*m*, ^3J = 6.4, 3.2, 1.2, H–C(4)); 2.73 (*dd*, ^2J = 18.9, ^3J = 0.9, *'endo'*-H–C(9)); 3.02 (*s*, MeO); 3.14 (*ddd*, ^3J = 6.8, 1.6, 1.2, H–C(3)); 5.52 (*dd*, ^3J = 5.8, 3.2, H–C(5)); 6.02 (*dd*, ^3J = 5.8, 2.8, H–C(6)). ^{13}C-NMR (100.62 MHz, $CDCl_3$; BB, DEPT): 13.78, 26.72, 31.14 (+, C(1), C(2), C(11)); 35.91, 42.33, 47.37 (+, C(4), C(7), C(8)); 38.25 (–, C(9)); 54.75 (+, MeO); 71.90 (+, C(3)); 133.97, 140.64 (+, C(5), C(6)); 204.08 (ϕ, C(10)). MS (70 eV): 191 (2.6, $[M + 1]^+$), 190 (19, $M^{+\cdot}$), 162 (5.3, $[M - CO]^+$), 159 (4.9, $[M - MeO]^+$), 158 (8.0, $[M - MeOH]^+$), 130 (20, $[M - CO - MeOH]^+$), 111 (100). HR-MS: 190.0998 ($C_{12}H_{14}O_2$, calc. 190.09937).

11-Hydroxytricyclo[5.4.0.0.^{4,8}]undeca-2,5-dien-10-one (**24**). A mixture of 1.0 g (6.32 mmol) of **10**, 25 ml of THF, 2 ml of H_2O, and 15 ml of CF_3COOH were refluxed for 1 h. The mixture was poured onto 100 ml of sat. $NaHCO_3$ soln. and extracted with 200 ml of Et_2O, the extract washed 3 times with 50 ml of sat. $NaHCO_3$ soln. 30 ml of H_2O and brine, dried ($MgSO_4$), and evaporated. The crude product (912 mg) was purified by CC (20 g SiO_2, Et_2O/pentane 1:2): 830 mg (74.5%) of **24**. A sample was crystallized from hexane. M.p. 62°. IR (KBr): 3440 (OH), 3090, 3040, 2940, 2900, 2875, 1690 (CO), 1387, 1362, 1326, 1304, 1245, 1233, 1218, 1159, 1113, 1053, 1028, 975, 959, 920, 893, 854, 780, 752, 739, 681, 615, 600, 565, 436. ^{1}H-NMR (270 MHz, $CDCl_3$): 2.46 (*m*, 1 H); 2.66 (*m*, 6 H); H–C(1), H–C(4), H–C(7), H–C(8), 2 H–C(9, OH); 3.96 (*d*, H–C(11)); 5.52 (*ddd*, H–C(2)); 5.72 (*dd*, H–C(6)); 6.13 (*ddd*, H–C(3)); 6.51 (*dd*, H–C(5)). ^{13}C-NMR (100.62 MHz, $CDCl_3$; BB, DEPT): 38.12 (–, C(9)); 34.47, 40.43, 44.02, 44.24 (+, C(1), C(4), C(7), C(8)); 73.65, (+, C(11); 126.96, 130.09, 134.60, 143.61 (+, C(2), C(3), C(5), C(6)); 213.2 (ϕ, C(10)). MS (70 eV): 177 (4.7, $[M + 1]^+$), 176 (38, $M^{+\cdot}$), 158 (8.1, $[M - H_2O]^+$), 147 (17, $[M - HCO]^+$), 133 (15, $[M - MeO]^+$), 129 (28, $[M - HCO - H_2O]^+$), 98 (100). HR-MS: 176.08372 (M^+, calc. 176.08372). Anal. calc. for $C_{11}H_{12}O_2$ (176.2): C 74.98, H 6.86; found: C 75.12, H 6.75.

Photolysis of **19a**. At –30°, 200 mg (1.28 mmol) of **19a** in 150 ml of pentane were photolyzed under N_2 for 105 min in a 150-ml falling-film photolysis apparatus, equipped with a quartz immersion well and a 150-W mercury lamp. The solvent was evaporated and the residue analyzed by GLC (25 m *OV 101*, 140°): **27**: rel. R_t 1.00, rel. amount 27%; **26**: R_t 1.17, 43%; **19a**: R_t 1.73, 29%. The product was separated with considerable losses by prep. GLC (1.5 m *SE 54*, 60°) to yield 5 mg (2.5%) of *10-methylidenetetracyclo[5.4.0.0^{4,8}.0^{9,11}]undeca-2,5-diene* (**27**) und 10 mg (5%) of *10-methylidenepentacyclo[5.4.0.0^{2,11}.0^{3,9}.0^{4,8}]undec-5-ene* (**26**; 95%, GLC).

27: ^{1}H-NMR (270 MHz, C_6D_6): 1.65 (*dm*, ^3J = 7.1, H–C(9)); 2.25 (*m*, H–C(4)); 2.29 (*dm*, ^3J = 7.1, H–C(11)); 2.34 (*m*, H–C(1)); 2.63 (*m*, H–C(8)); 2.67 (*m*, H–C(7)); 5.43 (*m*, 1 H); 5.47 (*m*, 1 H, =CH_2); 5.49 (*dddd*, ^3J = 9.4, 5.2, ^4J = 1.2, 0.7, H–C(2)); 5.55 (*ddd*, ^3J = 5.7, 3.2, ^4J = 0.7, H–C(6)); 5.85 (*dddd*, ^3J = 9.4, 5.5, ^4J = 1.4, 0.6, H–C(3)); 6.48 (*dd*, ^3J = 5.7, 2.8, H–C(5)). ^{13}C-NMR (100.62 MHz, C_6D_6; BB, DEPT): 19.44, 32.89, 39.89, 44.59, 45.80, 56.09 (+, C(1), C(4), C(7), C(8), C(9), C(11)); 105.02 (–, =CH_2); 128.35, 132.04, 132.64, 145.83 (+, C(2), C(3), C(5), C(6)); 140.04 (ϕ, C(10)). MS (70 eV): 157 (2.8, $[M + 1]^+$), 156 (23, $M^{+\cdot}$), 91 (100).

26: ^{1}H-NMR (270 MHz, C_6D_6): 1.10 (*tm*, ^3J = 7.8, H–C(1)); 1.54 (*m*, H–C(2)); 1.85 (*ddd*, ^3J = 6.6, 4.4, ^4J = 1.0, H–C(11)); 2.48 (*td*, ^3J_t = 5.4, ^3J_d = 2.8, H–C(4)); 2.55–2.75 (*m*, H–C(3), H–C(8), H–C(9)); 2.84 (*m*, H–C(7)); 4.89 (*d*, ^2J = 1.8, 1 H), 4.94 (*d*, ^2J = 1.8, 1 H; =CH_2); 5.73 (*dd*, ^3J = 5.4, 2.8, H–C(5)); 6.20 (*dd*, ^3J = 5.4, 2.4, H–C(6)). ^{13}C-NMR (100.62 MHz, C_6D_6; BB; DEPT, C,H correlation): 22.21 (+, C(2)); 23.24 (+, C(1)); 29.67 (+, C(11)); 39.58, 41.81, (+, C(8), C(9)); 40.95 (+, C(7)); 43.73 (+, C(4)); 51.16 (+, C(3)); 101.37 (–, C=*C*H_2); 130.97 (+, C(5)); 144.55 (+, C(6)); 152.32 (ϕ, C(10)). MS (70 eV): 157 (2.1, $[M + 1]^+$), 156 (16, $M^{+\cdot}$), 91 (100).

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