Preparation and Properties of 9-Methylenetricyclo[4.3.0.0^{3,8}]non-4-ene

Rolf Gleiter,* Thilo Herb, and Holger Lange

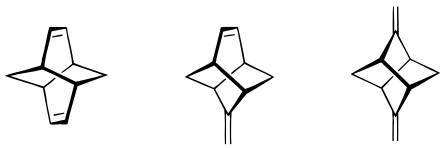
Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received July 31, 1996[⊗]

Several attempts to synthesize 9-methylenetricyclo[4.3.0.0^{3,8}]non-4-ene (**2**) are described, first by enlargement of the tricyclo[3.3.0.0^{3,7}]octane skeleton and second by reduction of the alcohol function in 9-methylenetricyclo[4.3.0.0^{3,8}]non-4-en-2-ol (**18**) and its derivative 5-methylene-11-phenyl-10, 12-dioxatetracyclo[7.3.0.0^{2,6}.0^{4,8}]dodecan-3-ol (**19**). Both routes proved to be unsuccessful. The synthesis of **2** could be achieved by ring opening of 7-methyl-3,8-dioxapentacyclo[4.4.1.0^{2,4}.0^{5,9}.0^{7,10}]-undecane (**26**) with Li in EDA to yield 9-methyltricyclo[4.3.0.0^{3,8}]nonane-4,9-diol (**27**). By using the Swern reagent, **27** could be transformed in a one-pot reaction to 9-methylenetricylo[4.3.0.0^{3,8}]-nonan-4-one (**31**), which yielded **2** via a Shapiro reaction. The PE spectra of **2** and **18** reveal an energy splitting of the π bands by about 1 eV. This splitting has been analyzed with the aid of HF−SCF calculations. A considerable interaction between the central six-membered ring and the double bonds in **2** and **18** has been found.

Introduction

The three molecules tricyclo[4.4.0.0^{3,8}]deca-4,9-diene (**1**, twistadiene), 9-methylenetricyclo[4.3.0.0^{3,8}]non-4-ene (**2**, twistbrenda-4,9-diene), and 2,6-dimethylenetricyclo-[3.3.0.0^{3,7}] octane (**3**, stella-2,6-diene) are structural isomers. They can formally be converted into each other



1 **2** **3**

by turning an *endo* double bond into an *exo* double bond and vice versa. Compounds **1** and **3** have been prepared not too long ago[1,2] while **2** is still unknown. All three are of interest because they are hydrocarbons in which two double bonds interact via a central cyclohexane ring that is held in a twist conformation.[3] In Figure 1 we show the filled π MOs of **1** and the two σ MOs of the central six-membered ring that have the correct symmetry to interact with them. This π/σ interaction is responsible for the sizeable split of the π bands in the PE spectra of **1** and **3**. It was reported that the energy difference of the π bands amounts to 1.3 eV in **1**[4] and 0.9 eV in **3**.[4] The missing number of this series is **2**, and so we embarked in the synthesis of this hydrocarbon.

Synthesis of 2. A problem in the synthesis of highly strained systems such as **1**−**3** is rearrangements, especially if carbocationic intermediates are involved.[5] Therefore we designed our synthesis of **2** to minimize the possibility of rearrangements.

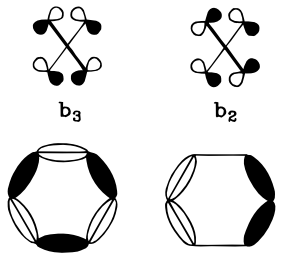


Figure 1. Comparison between the π MOs of **1** and the corresponding σ MOs of a twisted six-membered ring (ribbon orbitals).

Our first approaches to prepare **2** started with studies to enlarge one bridge in stellanone (**4**)[6] (Scheme 1). As shown in this scheme, reacting stellanone with diazomethane[7] and olefin **6** with cyanazide[8] were both unsuccessful. Also the ring enlargement of **8** and **11** with several reagents[9] that were successful in the ring expansion of other ketones failed. Therefore we decided to synthesize the twistbrendane skeleton directly.

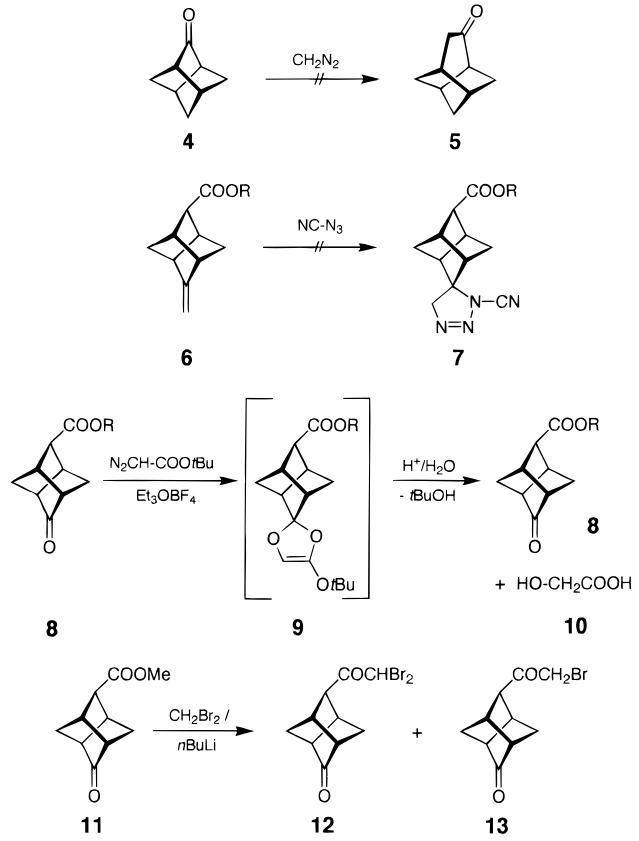
Our first synthesis commenced with a Diels−Alder reaction of 7,9-dioxa-8-phenylbicyclo[4.3.0]nona-2,4-diene (**14**)[10] with methyl vinyl ketone (**15**) to yield *anti*-10-acetyl-4-phenyl-3,5-dioxatricyclo[5.2.2.0^{2,6}]undec-8-ene (**16**)[11] (Scheme 2). To construct the pentacyclic system of **17**, we used the Paterno−Büchi reaction. This reaction has been used in related systems by Sauers et al.[12] and

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

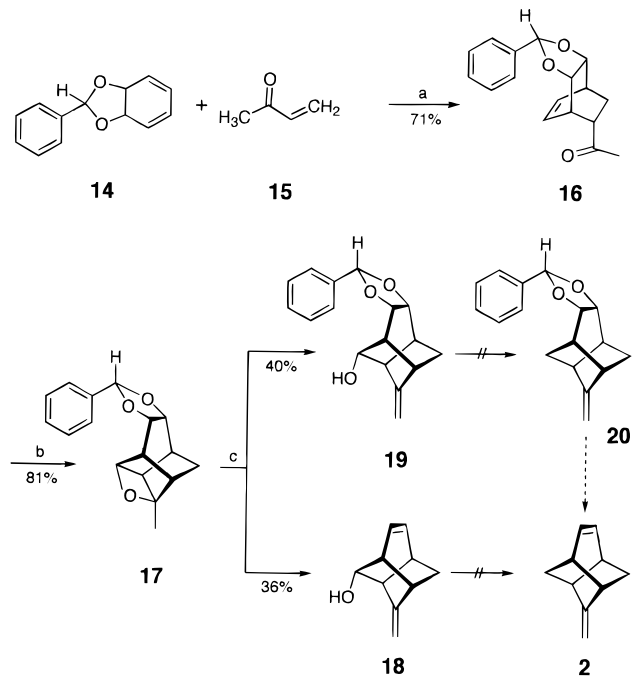
(1) Capraro, H.-G.; Ganter, C. *Helv. Chim. Acta* **1976**, *59*, 97.
(2) Kissler, B.; Gleiter, R. *Tetrahedron Lett.* **1985**, *26*, 185.
(3) (a) Review: Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369. (b) Borzyk, O.; Herb, T.; Sigwart, C.; Gleiter, R. *Pure Appl. Chem.* **1996**, *68*, 233.
(4) Gleiter, R.; Kissler, B.; Ganter, C. *Angew. Chem.* **1987**, *99*, 1292; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1252.
(5) Sauers, R. R.; Sickles, B. R. *Tetrahedron Lett.* **1970**, 1067. Sauers, R. R.; O'Hara, E. M. *J. Am. Chem. Soc.* **1974**, *96*, 2510. Sauers, R. R.; Weston, C. A.; Dentz, B. I. *J. Org. Chem.* **1980**, *45*, 2813.
(6) Nakazaki, M.; Naemura, K.; Arashiba, N. *J. Org. Chem.* **1978**, *45*, 888. Sauers, R. R.; Kelly, K. W.; Sickles, B. R. *J. Org. Chem.* **1972**, *37*, 537.
(7) Nakazaki, M.; Naemura, K.; Hashimoto, M. *J. Org. Chem.* **1983**, *48*, 2289.
(8) McMurry, J. E.; Coppolino, A. P. *J. Org. Chem.* **1973**, *38*, 2821.
(9) Regitz, M.; Hocker, J.; Liedhegener, A. *Organic Synthesis;* Wiley: New York, 1973; Collect. Vol. V, p 179. Mock. W. L.; Hartman, M. E. *J. Org. Chem.* **1977**, *42*, 459. Mock, W. L.; Hartman, M. E. *J. Am. Chem. Soc.* **1970**, *92*, 5767. Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 3010. Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 6510. Taguchi, H.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1972**, 4661. Taguchi, H.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1592.
(10) Yang, N. C.; Chen, M. J.; Chen, P.; Mak, K. T. *J. Am. Chem. Soc.* **1982**, *104*, 853. Yang, N. C.; Chen, M. J.; Chen, P. *J. Am. Chem. Soc.* **1984**, *106*, 7310.
(11) Gleiter, R.; Herb, T.; Borzyk, O.; Hyla-Kryspin, I. *Liebigs Ann. Chem.* **1995**, 357.

S0022-3263(96)01462-4 CCC: $12.00

Scheme 1



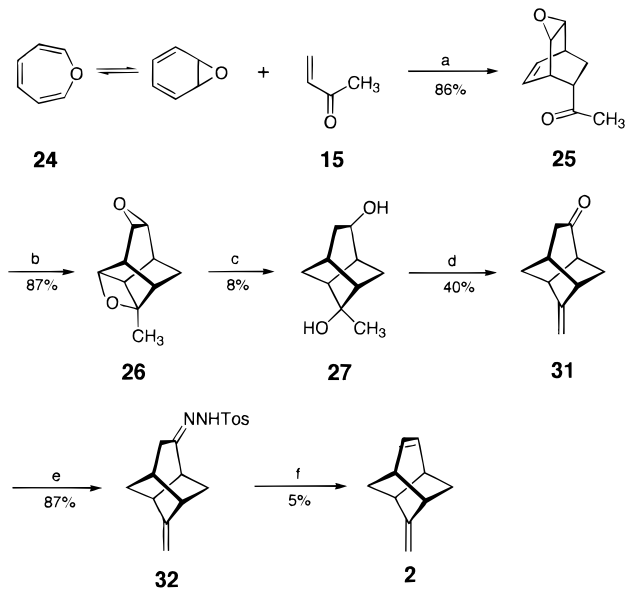
Scheme 2[a]



[a] Reagents and conditions: (a) rt., 5 days, neat; (b) *hν* (282 nm), Et_2O, 18 h; (c) *n*-BuLi, LDA, THF, rt., 20 h.

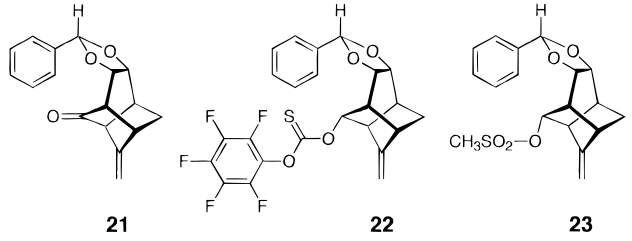
Nakazaki et al.[13] Irradiation of **16** yielded 1-methyl-7-phenyl-2,6,8-trioxapentacyclo[8.2.1.0^{3,13}.0^{4,12}.0^{5,9}]-tridecane (**17**).[11] By treating **17** with *n*-BuLi/LDA, a 1:1 mixture of 9-methylenetricyclo[4.3.0.0^{3,8}]non-4-en-2-ol (**18**) and 5-methylene-11-phenyl-10,12-dioxatetracyclo-[7.3.0.0^{2,6}.0^{4,8}]dodecan-3-ol (**19**) was obtained.[11] The latter species can be converted into **18** by treating it again with

Scheme 3[a]



[a] Reagents and conditions: (a) rt., 60 h, neat; (b) *hν* (282 nm), Et_2O, 40 h; (c) Li, EDA, rt, (d) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −60 °C; (e) $H_2NNHTos$, EtOH, rt, 3 days; (f) THF, *n*-BuLi, −10 °C.

n-BuLi. We transformed the alcohol **19** into the tetracyclic compounds **21**, **22**, and **23**.[14] But all our attempts



to prepare **20** from one of these twistbrendane derivatives failed. The same efforts for **18** were also undertaken in vain.

Our third attempt to obtain **2** used the same strategy as the second but with a slightly different intermediate. The protected twistbrendane skeleton was constructed by reacting oxepine (**24**)[15] with methyl vinyl ketone (**15**) (Scheme 3). The irradiaton of **25** afforded in good yields 7-methyl-3,8-dioxapentacyclo[4.4.1.0^{2,4}.0^{5,9}.0^{7,10}]undecane (**26**) in one step. Treatment of **26** with lithium in ethylenediamine (Li/EDA)[16] gave four products, 9-methyltricyclo[4.3.0.0^{3,8}]nonane-4,9-diol (**27**, 8%), 5-methyl-4-oxatetracyclo[4.3.1.0^{2,5}.0^{3,7}]decan-9-ol (**28**, 7%), 9-meth-

(12) Sauers, R. R.; Whittle, J. A. *J. Org. Chem.* **1969**, *34*, 3579. Sauers, R. R.; Schinski, W.; Mason, M. M. *Tetrahedron Lett.* **1969**, 79. Sauers, R. R.; Rousseau, A. D. *J. Am. Chem. Soc.* **1972**, *94*, 1776. Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850. Sauers, R. R.; Lynch, D. C. *J. Org. Chem.* **1980**, *45*, 1286.

(13) Nakazaki, M.; Naemura, K.; Kondo, Y. *J. Org. Chem.* **1976**, *41*, 1229. Nakazaki, M.; Naemura, K.; Harita, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1907. Nakazaki, M.; Naemura, K.; Harada, H.; Narutaki, H. *J. Org. Chem.* **1982**, *47*, 3470.

(14) Borzyk, O. Dissertation, Universität Heidelberg, Heidelberg, Germany, 1994.

(15) Gillard, J. R.; Newlands, M. J.; Bridson, J. N.; Burnell, D. J. *Can. J. Chem.* **1991**, *69*, 1337.

(16) Gleiter, R.; Borzyk, O. *Angew. Chem.* **1995**, *107*, 1094; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1001. Sauers. R. R.; Schinski, W.; Mason, M. M.; O'Hara, E.; Byrne, B. *J. Org. Chem.* **1973**, *38*, 642. Brown, H. C.; Ikegami, S.; Kawakami, J. H. *J. Org. Chem.* **1970**, *35*, 3243.

(17) Omura, K.; Swern. D. *Tetrahedron* **1978**, *34*, 1651. Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.

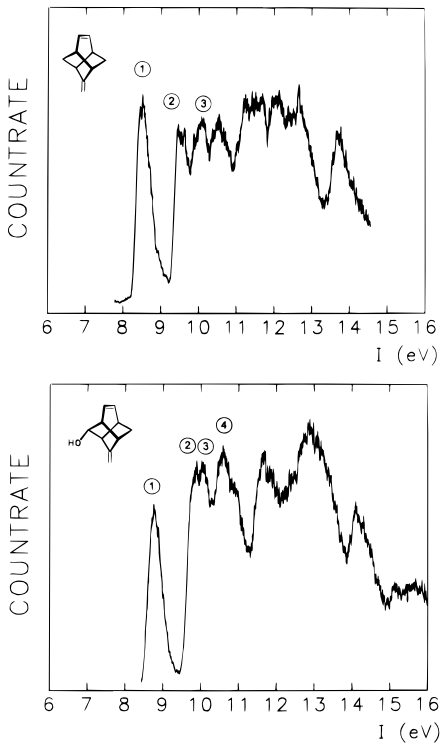


Figure 2. He I PE spectra of **2** and **18**.

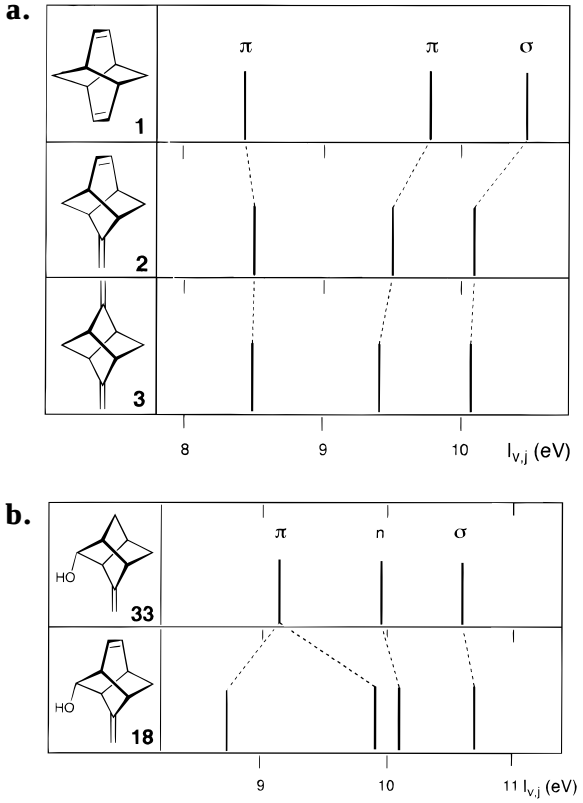
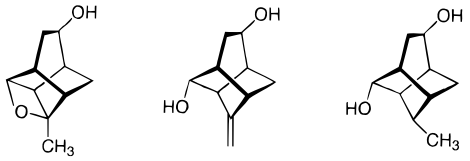


Figure 3. (a) Correlation between the first ionization energies of **1**−**3** (top). (b) Correlation between the first ionization energies of **33** and **18** (bottom).

ylenetricyclo[4.3.0.0^{3,8}]nonane-2,5-diol (**29**, 29%), and 9-methyltricyclo[4.3.0.0^{3,8}]nonane-2,5-diol (**30**, 46%), which could be separated by column chromatography on silica gel, using ether as the solvent.

The different solubilities of **27**−**30** in chloroform were of further help in the purifying process. Compounds **27**



28 **29** **30**

and **30** were nearly insoluble in $CHCl_3$ while **28** and **29** were soluble, and this difference was also helpful in the purification of **27**−**30**. Using the Swern reagent, we could oxidize the secondary hydroxyl group in **27** and simultaneously dehydrate the tertiary alcohol in a one-pot reaction[18] to yield 9-methylenetricyclo[4.3.0.0^{3,8}]nonan-4-one (**31**) (Scheme 3). The final steps from **31** to **2** involved formation of tosylhydrazone **32**, followed by a Shapiro elimination.[19]

Photoelectron Spectra of 2 and 18. As stated in the introduction, **2** and, to a lesser extent, **18** are good molecules in which to examine the interaction between an endocyclic and an exocyclic double bond via a twisted six-membered ring. To study this interaction, we used He I PE spectroscopy. The PE spectra of **2** and **18** each show two bands below 10 eV (Figure 2) which we assign to ionization processes from predominantly π MOs. The assignment of the bands in the PE spectrum of **2** is supported by the positions of the bands in **1** and **3** (Figure 3a). In the case of **18**, comparison for PE data of the alcohol **33** is useful (Figure 3b).

Table 1. Comparison between the Recorded Vertical Ionization Energies, $I_{v,j}$, and the Calculated Orbital Energies, $-\epsilon_j$, of 2 and 18

compd	band	$I_{v,j}$	assignment	$-\epsilon_j$ (3-21G basis)
2	1	8.5	17b (π^-)	8.80
	2	9.5	16b (π^+)	9.93
	3	10.1	15b (σ)	10.84
18	1	8.70	40a (π^-)	9.04
	2	9.9	39a (π^+)	10.26
	3	10.1	38a (n)	10.92
	4	10.6	37a (σ)	11.54

To assign the observed PE bands to individual ionization processes, we assume the validity of Koopmans' theorem.[20] This approximation allows us to correlate the observed vertical ionization energies, $I_{v,j}$, with the calculated orbital energies, ϵ_j, of the ground state. To derive the orbital energies, we have carried out *ab initio* calculations at the Hartree−Fock (HF) SCF level of theory by using a 3-21G basis set.[21] The geometries of **2** and **18** were minimized within their point groups. The orbital energies at the optimized geometries are listed in Table 1 and compared to the recorded vertical ionization energies. The sequence of the MOs (π on top of σ MOs) corresponds to the empirical assigment given in

(18) Gleiter, R.; Herb, T.; Hofmann, J. *Synlett* **1996**, 987.
(19) Shapiro, R. H.; Heath, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 5734. Shapiro, R. H. *Org. React.* **1976**, *23*, 405.
(20) Koopmans, T. *Physica* **1934**, *1*, 104.
(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94, Revision D.2*; Gaussian, Inc.: Pittsburgh, PA, 1995.

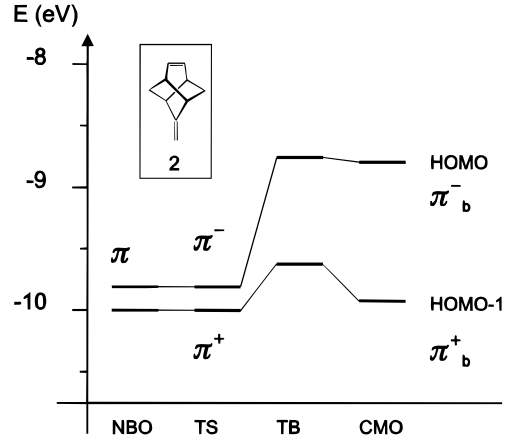


Figure 4. Through-space (TS)/through-bond (TB) interaction diagram of **2**. NBO: self-energy of the π NBOs. TS: energy after TS interaction. TB: energy after the interaction with the ribbon orbitals. CMO: energies of the 3-21G CMOs.

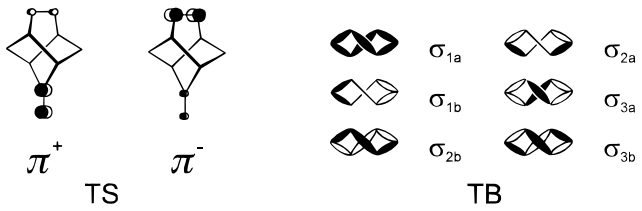


Figure 5. Schematic representation of the most important precanonical MOs of **2**. At left the b(π^+) and b(π^-) linear combinations after through-space interaction. At right the six ribbon orbitals of the central six-membered ring in **2**.

Figure 3. The calculated energy difference between the π MOs is close to the split found in the PE experiment for **2** and **18**.

To determine the size of the through-space (TS) and through-bond (TB) interactions, we used a methodology, first suggested by Heilbronner and Schmelzer,[22] which is based on the Fock matrix in a localized basis of the one-electron wave functions. The first step is the transformation of the canonical HF orbitals (CMOs) into a set of localized MOs by means of the Weinhold natural bond orbital localization procedure,[23] which leads to the natural bond orbitals (NBOs). The matrix elements of the nondiagonal Fock matrix, $\mathbf{F}^{NBO}$, now have the following meaning: (a) each diagonal element, F_{ii}^{NBO}, is the energy of the i-th NBO ϕ_i and (b) each off diagonal element, F_{ij}^{NBO}, is a measure for the interaction energy between the NBOs ϕ_i and ϕ_j. For a quantitative treatment we apply the procedure of Imamura et al.[24]

Figure 4 shows schematically the results. On the left-hand side are the energies of the two localized π NBOs of **2**. They are split because π^+ is mainly localized at the exocyclic double bond, whereas π^- is mainly localized on the endocyclic one (Figure 5). The through-space interaction does not affect the splitting between them due to the large distance between both π bonds, $d = 3.3$ Å. The TB interaction occurs via the ribbon orbitals (see Figure 1) of the central, twisted, six-membered ring. This leads to a considerable splitting (0.9 eV) due to a strong interaction between the ribbon orbital σ (3b) and π^- (see Figure 5). This analysis is supported by the finding that in **2** the σ character of the HOMO amounts to 20%, while for the HOMO − **1** it is calculated to be only 8%. It is interesting to note that the π splitting of the three compounds decreases in going from **1** to **3**, although the energy gap between the localized π orbitals and the ribbon orbital σ (3b) decreases too. The gap amounts to 3.5 eV in **1**, to 3.0 eV in **2**, and to 2.5 eV in **3**. This order can be traced back to the lowering of the σ (3b) energy, which is influenced by the decreasing stain energy. Simultaneously, the bond length of the central, cross-like-arranged C−C σ-bond is shortened from 1.62 Å in **3** to 1.61 Å in **2** and 1.60 Å in **1**. Our investigations demonstrate nicely that the interaction between σ (b) and an endocyclic π bond is stronger than the interaction between σ (b) and an exocyclic π bond. This "change" is the reason why the splitting decreases in the order **1** > **2** > **3** (see Figure 3a).

Experimental Section

The general reaction conditions and the instruments used were the same as described for the preparation of 2,9-dimethylenetricyclo[4.3.0.0^{3,8}]non-4-ene.[11] Microanalyses were carried out at the analytical section of the Chemische Institute der Universität Heidelberg. The photoelectron spectra of **2** and **18** were recorded with a PS 18 instrument from Perkin-Elmer (Beaconsfield) at rt. Calibration was performed with Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV on the $^3P_{3/2}$ Ar line was obtained.

***endo*-8-Acetyl-3-oxatricyclo[3.2.2.0^{2,4}]non-6-ene (25).** To magnetically stirred oxepine (**24**)[15] (9.2 g, 100 mmol) was added dropwise 11.2 g (160 mmol) of methyl vinyl ketone (**15**) at rt. The reaction mixture was stirred for 60 h and purified by column chromatography on silica gel with pentane/ether (4:1) as eluent to yield **25** (14.12 g, 86%) as a light yellow liquid: R_f (SiO_2, ether, *p*-methoxybenzaldehyde) = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62−1.81 (m, 2H), 2.11 (s, 3H), 2.61−2.67 (m, 1H), 3.01−2.99 (m, 1H), 3.20−3.27 (m, 2H), 3.33−3.35 (m, 1H), 5.67−5.72 (dd, $^3J_1 = 6.8$ Hz, $^3J_2 = 7.7$ Hz, 1H), 5.85−5.90 (dd, $^3J_1 = 7.2$ Hz, $^3J_2 = 7.6$ Hz, 1H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 25.02 (t), 28.54 (q), 32.91 (d), 35.78 (d), 47.97 (d), 48.22 (d), 48.29 (d), 125.03 (d), 129.32 (d), 207.84 (s); IR ($CDCl_3$) 3054, 3014, 2954, 2928, 2868, 2230, 1701, 1406, 1354, 1249, 1174, 830 cm^{-1}; UV/vis (*n*-pentane) λ_{max} [nm] (log ϵ) = 204 (2.56), 268 (1.48), 278 (1.50). Anal. Calcd for $C_{10}H_{12}O_2$ (164.2): C, 73.15; H, 7.37. Found: C, 73.20; H, 7.35.

7-Methyl-3,8-dioxapentacyclo[4.4.1.0^{2,4}.0^{5,9}.0^{7,10}]-undecane (26). A solution of **25** (5.0 g, 30 mmol) in 2.5 L of dry diethyl ether was degassed with a dry argon stream for 45 min. The solution was irradiated for 40 h with a high-pressure mercury immersion lamp (700 W) equipped with a special quartz M282 filter ($\lambda \geq 282$ nm, Fa. Peschl, Mainz, Germany). The crude oxetane **26** was obtained by evaporation of the ether at reduced pressure. The product was purified by column chromatography with pentane/ether (4:1) as eluent, yielding 4.36 g (87%) of **26** as a colorless oil which was crystallized from pentane/ether at −20 °C to give colorless crystals: mp = 37 °C; R_f (SiO_2, ether, *p*-methoxybenzaldehyde) = 0.39; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 3H), 1.57−1.61 (dd, $^2J = 12.2$ Hz, $^3J = 1.9$ Hz, 1H), 1.81−1.88 (ddd, $^2J = 12.2$ Hz, $^3J_1 = 6.2$ Hz, $^3J_2 = 1.6$ Hz, 1H), 2.09−2.12 (dm, $^3J = 6.2$ Hz, 1H), 2.18−2.23 (q, $^3J = 5.5$ Hz, 1H), 2.66−2.69 (m, 1H), 2.71−2.76 (m, 1H), 3.42−3.51 (m, 2H), 4.59−4.61 (dd, $^3J = 2.9$ Hz, 1H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 17.16 (q), 31.62 (d), 34.49 (t), 40.04 (d), 44.47 (d), 47.31 (d), 55.27 (d), 57.59 (d), 82.46 (d), 96.23 (s); MS *m/z* 164 (4) [M^+], 163 (2) [$M - 1^+$], 121 (47), 117 (20), 107 (12), 105 (12), 104 (22), 103 (60), 95 (21), 94 (36), 93 (35), 92 (22), 91 (100) [$C_7H_7^+$], 81 (23), 80 (24), 79 (64), 78 (41), 77 (84), 68 (14), 66 (37), 65 (29), 55 (21), 53 (16), 51(19); IR ($CDCl_3$) 2960, 2876, 1381, 1226, 1105, 993, 944, 887, 874, 861, 849, 831 cm^{-1}; UV/vis (*n*-pentane) λ_{max} [nm] (log ϵ) = 196 (3.08), 228 (2.31), 278 (1.84). Anal. Calcd for $C_{10}H_{12}O_2$ (164.20): C, 73.15; H, 7.37. Found: C, 73.05; H 7.31.

(22) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936.
(23) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066.
(24) Imamura, A.; Ohsaku, M. *Tetrahedron* **1981**, *37*, 2191.

Reduction of 7-Methyl-3,8-dioxapentacyclo[4.4.1.0^{2,4}.0^{5,9}.0^{7,10}]undecane (26) with Li/EDA. To a 1-L three-necked flask fitted with a reflux condenser and a magnetic stirring bar were added at rt with vigorous stirring 12 g (73 mmol) of oxetane **26** and 50 mL of anhydrous ethylenediamine (EDA), followed by 0.8 g (117 mmol) of lithium powder. The reduction is exothermic, and an ice bath was necessary to keep the temperature at 40 °C, where it was maintained for 30 min. Then an additional 3.2 g (467 mmol) of lithium powder was added. The reaction mixture was stirred for an additional 1 h at rt. Many colors were observed during the reduction, but the reduction was complete when a blue-purple color persisted. The reaction mixture was cooled, and 100 mL of diethyl ether and 150 mL of water were added to destroy excess reagent. The aqueous layer was extracted for 2 h with ether. The combined organic layers were dried with $MgSO_4$ and concentrated to give a brown oily residue. Purificaton by silica gel chromatography with diethyl ether as eluent gave a mixture of products. Additional purification of this mixture by silica gel column chromatography yielded **28** (0.85 g, 7%) as a colorless oil and **27** (1.03 g, 8%), **29** (3.52 g, 29%), and **30** (5.64 g, 46%) as white solids. **27** and **30** were recrystallized from $CHCl_3$.

9-Methyltricyclo[4.3.0.0^{3,8}]nonane-4,9-diol (27): mp = 160 °C; R_f (SiO_2, ethyl acetate, *p*-methoxybenzaldehyde) = 0.37; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.77−0.81 (d, ^2J = 11.0 Hz, 1H), 1.27 (s, 3H), 1.35−1.47 (dt, J_1 = 13.4 Hz, J_2 = 3.9 Hz, 2H), 1.50−1.52 (m, 1H), 1.60−1.61 (m, 1H), 1.72−1.75 (d, J = 9.6 Hz, 1H), 1.88−2.00 (m, 3H), 2.16−2.21 (dd, J_1 = 9.6 Hz, J_2 = 7.4 Hz, 1H), 3.88−3.93 (td, J_1 = 7.2 Hz, J_2 = 3.6 Hz, 1H), 4.44 (s, 1H), 4.69−4.70 (d, $^3J_1$ = 3.3 Hz, 1H); ^{13}C NMR (75.47 MHz, DMSO-d_6) δ 25.55 (q), 28.70 (t), 31.31 (t), 32.08 (d), 37.55 (t), 38.15 (d), 44.54 (d), 44.58 (d), 71.09 (d), 83.38 (s); MS: *m*/*z* 168 (0.04) [M$^+$], 150 (11) [M$^+$ − H_2O], 132 (8) [M$^+$ − 2H_2O], 117 (12) [C_9H_9], 109 (22), 107 (35), 106 (17), 95 (17), 93 (17), 92 (50), 91 (31), 81 (43), 80 (100) [C_6H_8], 79 (65) [C_6H_7], 78 (13), 77 (17), 72 (14), 71 (37), 67 (11), 53 (12); HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1149; IR (KBr) 3315, 2956, 2936, 1294, 1112, 1105, 1070 cm^{-1}; UV/vis (CH_3CN) λ_{max} [nm] (log ϵ) = 194 (2.62).

5-Methyl-4-oxatetracyclo[4.3.1.0^{2,5}.0^{3,7}]decan-9-ol (28): R_f (SiO_2, ethyl acetate, *p*-methoxybenzaldehyde) = 0.40; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10−1.17 (ddd, ^2J = 11.7 Hz, $^3J_1$ = 5.9 Hz, $^3J_2$ = 2.0 Hz, 1H), 1.32−1.45 (m, 2H), 1.41 (s, 3H), 1.56 (s, 1H), 1.87−1.90 (m, 1H), 1.95−1.99 (d, ^2J = 11.8 Hz, 1H), 2.10−2.12 (m, 1H), 2.18−2.22 (m, 1H), 2.39−2.44 (m, 1H), 4.55−4.57 (dd, $^3J_1$ = 1.8 Hz, $^3J_2$ = 5.4 Hz, 1H), 4.84−4.87 (dd, $^3J_1$ = 4.9 Hz, $^3J_2$ = 3.6 Hz, 1H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 23.72 (q), 25.87 (t), 32.05 (t), 36.17 (d), 38.57 (d), 47.48 (d), 56.35 (d), 78.98 (d), 81.48 (s), 84.04 (d); MS *m*/*z* 166 (19) [M$^+$], 148 (4) [M$^+$ − H_2O], 123 (38) [$C_8H_{11}O^+$], 122 (12) [$C_8H_{10}O^+$], 112 (10) [$C_6H_8O_2^+$], 107 (10) [$C_7H_7O^+$], 105 (22) [$C_8H_9^+$], 95 (14), 94 (10) [$C_6H_6O^+$], 93 (11) [$C_7H_9^+$], 91 (17), 87 (20), 81 (14), 80 (76), 79 (96) [$C_6H_7^+$], 78 (18), 77 (18), 73 (14), 69 (14), 67 (13), 43 (100); HRMS calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.1008; IR (KBr) 3393, 3359, 2978, 2959, 1377, 1304, 1146, 1127, 1079, 1018, 960, 946, 903, 890 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} [nm] (log ϵ) = 244 (1.70).

9-Methylenetricyclo[4.3.0.0^{3,8}]nonane-2,5-diol (29): mp = 144 °C; R_f (SiO_2, ethyl acetate, *p*-methoxybenzaldehyde) = 0.32; ^{1}H NMR (200 MHz, DMSO-d_6) δ 1.04−1.11 (dd, ^2J = 10.9 Hz, ^3J = 1.6 Hz, 1H), 1.16−1.26 (m, 1H), 1.43−1.52 (dd, ^2J = 13.7 Hz, ^3J = 3.6 Hz, 1H), 1.75−1.76 (m, 1H), 1.85−1.96 (ddd, ^2J = 13.7 Hz, $^3J_1$ = 7.3 Hz, $^3J_2$ = 1.9 Hz, 1H), 2.02−2.05 (m, 1H), 2.22−2.25 (m, 1H), 2.30−2.33 (m, 1H), 3.81−3.86 (dm, ^3J = 5.2 Hz, 2H), 4.25−4.29 (dd, $^3J_1$ = 2.2 Hz, $^3J_2$ = 5.2 Hz, 1H), 4.47 (s, 1H), 4.62 (s, 1H), 4.87 (d, ^3J = 3.0 Hz, 1H); ^{13}C NMR (50.32 MHz, DMSO-d_6) δ 31.99 (t), 35.64 (t), 38.47 (d), 38.73 (d), 41.51 (d), 48.34 (d), 69.85 (d), 71.97 (d), 97.85 (t), 160.20 (s); MS: *m*/*z* 166 (1) [M$^+$], 148 (7) [M$^+$ − H_2O], 120 (15) [$C_9H_{12}^+$], 119 (13) [$C_9H_{11}^+$], 117 (15) [$C_9H_9^+$], 105 (30) [$C_7H_5O_1^+$], 104 (19) [$C_8H_8^+$], 94 (10) [$C_7H_{10}^+$], 93 (50) [$C_7H_9^+$], 92 (34) [$C_7H_8^+$], 91 (52) [$C_7H_7^+$], 81 (32), 80 (100) [$C_6H_8^+$], 79 (71) [$C_6H_7^+$], 78 (33) [$C_6H_6^+$], 77 (32) [$C_6H_5^+$], 69 (10), 67 (11), 65 (10), 57 (19), 55 (11), 53 (12); HRMS calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.0968; IR (KBr) 3412, 2956, 2937, 1631, 1112, 1069 cm^{-1}; UV/vis (CH_3CN) λ_{max} [nm] (log ϵ) = 196 (3.16), 222 (2.04). Anal. Calcd for $C_{10}H_{14}O_2$ (166.1): C, 72.26; H, 8.49. Found: C, 72.01; H, 8.59.

9-Methyltricyclo[4.3.0.0^{3,8}]nonane-2,5-diol (30): mp = 155 °C; R_f (SiO_2, ethyl acetate, p-methoxybenzaldehyde) = 0.29; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.75−0.78 (d, ^2J = 11.5 Hz, 1H), 0.88−0.90 (d, ^3J = 6.9 Hz, 3H), 1.36−1.42 (dd, ^2J = 13.5 Hz, ^3J = 3.5 Hz, 1H), 1.56−1.63 (dd, ^2J = 11.5 Hz, ^3J = 7.9 Hz, 1H), 1.67 (m, 1H), 1.76−1.77 (m, 2H), 1.83−1.90 (ddd, ^2J = 13.5 Hz, $^3J_1$ = 7.4 Hz, $^3J_2$ = 1.7 Hz, 1H), 1.93−1.97 (m, 1H), 2.77−2.83 (q, ^3J = 6.9 Hz, 1H), 3.80−3.84 (dd, ^3J = 3.4 Hz, 1H), 4.25 (m, 1H), 4.44 (d, ^3J = 3.6 Hz, 1H), 4.75 (d, ^3J = 2.9 Hz, 1H); ^{13}C NMR (75.47 MHz, DMSO-d_6) δ 14.94 (q), 28.08 (t), 36.29 (t), 37.95 (d), 38.16 (d), 38.85 (d), 42.10 (d), 48.31 (d), 70.63 (d), 73.91 (d); MS: *m*/*z* 150 (5) [M$^+$ − H_2O], 135 (5) [M$^+$ − H_2O, CH_3], 121 (13), 106 (12) [$C_8H_{10}^+$], 96 (23), 95 (34), 94 (17), 93 (44) [$C_7H_9^+$], 92 (13), 91 (24), 81 (36), 80 (100) [$C_6H_8^+$], 79 (60) [$C_6H_7^+$], 78 (13), 77 (23), 72 (57), 71 (60), 67 (20), 57 (16), 55 (21), 53 (12); HRMS calcd for $C_{10}H_{14}O_1$ [M$^+$ − H_2O] 150.1045, found 150.1050; IR (KBr) 3330, 2943, 1361, 1081, 1066, 1002, 990, 964 cm^{-1}; UV/vis (CH_3CN) λ_{max} [nm] (log ϵ) = 194 (2.48).

9-Methylenetricyclo[4.3.0.0^{3,8}]nonan-4-one (31). To a stirred solution of oxalyl chloride (3.0 mL, 33.3 mmol) in dry CH_2Cl_2 (270 mL) was added dry DMSO (5.0 mL, 66.6 mmol) at −60 °C. After the solution was stirred for 2 min at −60 °C, 1.4 g (8.32 mmol) of **27** in 60 mL of dry CH_2Cl_2 was added. The mixture was stirred for 15 min at −60 °C, treated with triethylamine (23.4 mL, 155.5 mmol) and then allowed to warm up to rt before being poured into cold water (150 mL). The aqueous layer was extracted twice with CH_2Cl_2. The combined CH_2Cl_2 solutions were washed three times with cold aqueous HCl (2%) and twice with H_2O, saturated aqueous $NaHCO_3$, and brine, the solution was dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by silica gel column chromatography with pentane/ether (4:1) as eluent yielding 494 mg (40%) of **31** as a white solid: mp = 42 °C; R_f (SiO_2, pentane/ether, 1:1, *p*-methoxybenzaldehyde) = 0.48; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17−1.24 (dt, ^2J = 12.2 Hz, ^3J = 1.4 Hz, 2H), 1.64−1.75 (dd, J_1 = 5.2 Hz, J_2 = 1.8 Hz, 2H), 1.84−1.88 (dd, ^2J = 12.2 Hz, ^3J = 1.8 Hz, 1H), 2.03−2.10 (dd, ^2J = 17.1 Hz, ^3J = 3.4 Hz, 1H), 2.51−2.71 (m, $^2J_1$ = 17.1 Hz, $^2J_2$ = 12.6 Hz, 4H), 4.55 (s, 1H), 4.60 (s, 1H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 28.63 (d), 33.21 (t), 39.99 (d), 40.08 (t), 42.25 (d), 42.38 (t), 47.58 (d), 95.64 (t), 160.17 (s), 215.26 (s); MS *m*/*z* 148 (18) [M$^+$], 133 (5) [M$^+$ − CH_3], 120 (18) [M$^+$ − CO], 106 (11), 105 (26) [M$^+$ − CO − CH_3], 104 (18), 92 (30), 91 (61) [M$^+$ − C_3H_5O], 80 (14), 79 (100) [$C_6H_7^+$], 78 (75), 77 (52), 69 (24), 65 (13), 55 (18), 53 (12), 51 (16); IR (neat film) 2964, 1731, 1681, 1261, 1075, 1020, 784, 759 cm^{-1}; UV/vis (*n*-pentane) λ_{max} [nm] (log ϵ) = 198 (2.86), 294 (2.52), 306 (2.67), 320 (2.64), 334 (2.27), 352 (2.12). Anal. Calcd for $C_{10}H_{12}O$ (148.2): C, 81.04; H, 8.16. Found: C, 81.09; H 8.15.

(9-Methylentricyclo[4.3.0.0^{3,8}]non-4-eneyl)tosylhydrazone (32). To a magnetically stirred solution of 499 mg (3.37 mmol) of ketone **31** in 20 mL of anhydrous ethanol was added 648 mg (3.48 mmol) of *p*-toluenesulfonohydrazide. The reaction mixture was stirred for 3 days at rt. The light brown needles were collected by filtration and dried. The liquid was evaporated. Purification of the residue by silica gel column chromatography (elution with pentane/ether, 3:1) gave further product. The yield of tosylhydrazone **32** was 928 mg (87%): mp 181 °C; R_f (SiO_2, pentane/ether, 1:1, *p*-methoxybenzaldehyde) = 0.21; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91−0.95 (d, ^2J = 11.2 Hz, 1H), 1.47−1.51 (d, ^2J = 11.2 Hz, 1H), 1.52−1.58 (m, 1H), 1.64−1.77 (m, 2H), 2.15−2.21 (md, ^2J = 15.7 Hz, 2H), 2.28−2.33 (dd, ^2J = 16.3 Hz, ^3J = 3.3 Hz, 1H), 2.41 (s, 3H), 2.43−2.47 (d, ^2J = 11.8 Hz, 1H), 2.56−2.58 (d, ^3J = 5.8 Hz, 1H), 2.65−2.69 (t, ^3J = 5.7 Hz, 1H), 4.46 (s, 1H), 4.49 (s, 1H), 7.26−7.31 (dd, J_1 = 8.3 Hz, J_2 = 6.9 Hz, 2H), 7.81−7.84 (d, J_1 = 8.3 Hz, 2H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 21.57 (q), 28.60 (d), 31.15 (t), 34.80 (t), 39.39 (t), 40.48 (d), 40.57 (d), 42.82 (d), 95.10 (t), 127.94 (d), 129.55 (d), 135.69 (s), 143.88 (s), 160.59 (s), 166.00 (s); MS *m*/*z* 316 (0.2), 175 (23), 161 (20), 144 (13), 133 (20), 132 (10), 131 (17), 119 (10), 117 (32), 115 (11), 107 (11), 105 (30), 104 (12), 103 (24), 99 (11), 97 (16), 95 (16), 93

(20), 92 (17), 91 (88) [$C_7H_7^+$], 85 (41), 83 (22), 81 (23), 80 (29), 79 (47), 78 (18), 77 (32), 75 (15), 71 (47), 70 (12), 69 (19), 67 (16), 65 (18), 58 (11), 57 (100), 56 (15), 55 (33), 53 (13); HRMS calcd for $C_{17}H_{20}O_2N_2S$ 316.1245, found 316.1206; IR (KBr) 3439, 3216, 2957, 1696, 1646, 1493, 1405, 1335, 1169, 1028 cm^{-1}; UV/vis (CH_3CN) λ_{max} [nm] (log ϵ) = 198 (4.21), 226 (3.93).

9-Methylentricyclo[4.3.0.0^{3,8}]non-4-ene (2). A mixture of 662 mg of tosylhydrazone **32** in 50 mL of dry THF was stirred at −10 °C for 15 min. A 1.6 M solution of *n*-butyllithium (5.3 mL, 1.38 mmol) in hexane was added over the course of 15 min. The mixture was allowed to warm to rt over 2 h. Then 50 mL of water was added carefully to destroy the excess *n*-butyllithium. The aqueous layer was extracted twice with ether. The combined organic solutions were washed with brine and dried with $MgSO_4$, and the solvent was evaporated carefully at 0 °C. The residue was chromatographed on silica gel (elution with pentane) to yield **2** (14 mg, 54%) which could be crystallized at −20 °C as colorless needles: R_f (SiO_2, pentane, iodine) = 0.51; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.88−0.93 (dd, ^2J = 9.6 Hz, ^3J = 1.9 Hz, 2H), 1.65−1.74 (dd, ^2J = 9.6 Hz, ^3J = 6.4 Hz, 2H), 2.28−2.32 (m, 2H), 2.67−2.72 (m, 2H), 4.40 (s, 2H), 6.31−6.35 (dd, J = 3.4 Hz, J = 4.6 Hz, 2H); ^{13}C NMR (50.32 MHz, CD_2Cl_2) δ 35.95 (d), 38.08 (d), 46.29 (t), 92.08 (t), 136.84 (d), 162.84 (s); MS *m*/*z* 132 (53) [M^+], 131 (22), 117 (85), 116 (13), 115 (32), 104 (34), 103 (11), 91 (73), 79 (57), 78 (100) [$C_6H_6^+$], 77 (42), 65 (16), 63 (10), 54 (18), 53 (12), 52 (10), 51 (24); IR (CD_2Cl_2) 3047, 2962, 2933, 2857, 1681, 1458, 1294, 1257, 876 cm^{-1}; UV/vis (*n*-pentane) λ_{max} [nm] (log ϵ) = 198 (2.59), 230 (1.93).

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft, Ludwigshafen, for financial support. H.L. thanks the Studienstiftung des Deutschen Volkes for a stipend.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of **27**−**30**, **32**, and **2** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO961462R