3-Methylenetricyclo[3.1.0.0^{2,6}]hexane, a Tricyclic Isomer of Toluene: Synthesis and Addition onto Tetracyanoethylene

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A multistep ring-contraction route starting from tricyclo[4.1.0.0^{2,7}]heptan-3-one (**1**) resulted in a mixture of the title compound **7** and the homofulvene **8** in a ratio of 1:2.5. In a second synthesis, a 3.5:1 mixture of **7** and three additional hydrocarbons was obtained from 4-(phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexan-3-one (**9**) in a two-step sequence. On being heated at 175 °C in solution, **7** rearranged to toluene. Treatment of **7** with tetracyanoethylene gave rise to a 1:5 mixture of the [2+2] cycloadduct **16** and the cyclopropadicyclopentene derivative **17**.

Introduction

Detailed knowledge of thermal isomerisations of strained hydrocarbons provides information about the strength of chemical bonds, the magnitude of strain energies, and the rules governing bond reorganisations.[1] Our previous studies have been focused on strained methylenebicycloalkenes[2] and *endo*,*endo*-bridged bicyclo[1.1.0]butanes.[3] The presence of both an olefinic methylene group and a bicyclo[1.1.0]butane system within a molecule results in a special situation, particularly if these subunits are in conjugation with each other. One compound of that kind has already been investigated: 3-methylenetricyclo[4.1.0.0^{2,7}]heptane,[4] the higher homologue of the title compound **7**. The structure of the major product, as well as the activation parameters,[4] fit smoothly with the results of the thermal rearrangement of tricyclo[4.1.0.0^{2,7}]heptane and a series of its derivatives, which are believed to occur in two consecutive concerted steps.[3b] In the case of **7**, such a mechanism should be impeded if not impossible, due to the reduction of the ring size by one methylene group. We therefore undertook to investigate **7**, and report here on the synthesis of **7** and its reaction with tetracyanoethylene (TCNE), while the thermolysis of **7** in the gas phase is the subject of a forthcoming article.[5] The preparation of a pentamethyl derivative of **7** from hexamethyl Dewar benzene and its addition onto TCNE was published some time ago by Hogeveen et al.[6]

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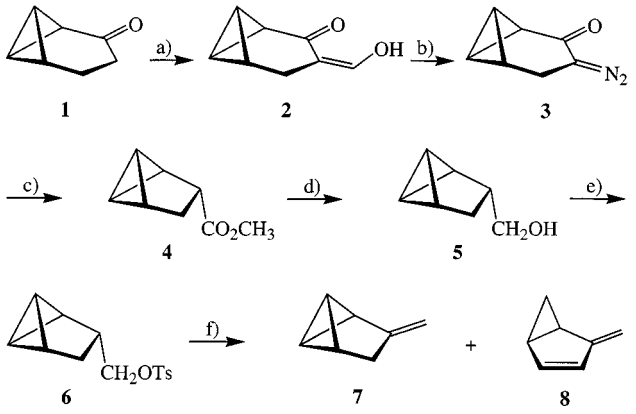
Results and Discussion

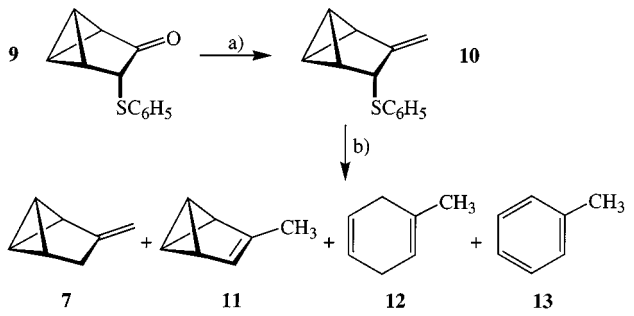
1. Synthesis of 7 by Ring-Contraction of Tricyclo[4.1.0.0^{2,7}]heptan-3-one (1)

Synthetic access to highly strained compounds has often been achieved by ring-contraction of higher homologues, which are usually much less strained and much more easily available.[7] In particular, the light-induced[8] Wolff rearrangement[9−12] of cyclic α-diazo ketones[13] to form ketene intermediates,[14] which can instantaneously be trapped by alcohols to give the pertinent contracted carboxylic esters, has proved to be of special value in this respect.[15] Thus, in our hands, bicyclo[3.2.0]hept-6-en-2-one could successfully be transformed into methyl bicyclo[2.2.0]hex-5-ene-2-carboxylate.[2d] As a feasible synthetic route to **7**, we therefore envisaged an analogous multistep sequence starting from the known tricycloheptanone **1** (Scheme 1).

The tricyclic ketone **1**, prepared by photolytic oxadi-π-methane rearrangement from bicyclo[3.2.0]hept-6-en-2-one,[16] was formylated in diethyl ether, with the use of a large excess of ethyl formate, to give **2**. Without purification, the activated ketone **2** was subjected to diazo group transfer,[17] using *p*-toluenesulfonyl azide[18] as the reagent. Formation of **3**, obtained in about 43−62% yield relative to starting ketone **1**, was indicated by strong absorption bands in the infrared spectrum at 2085 and 1635 cm^{-1}, typical of an α-diazo ketone.[19] By irradiating **3** in methanol, through a Pyrex filter, we obtained the ring-contracted ester **4**. Reduction of this with $LiAlH_4$ provided the alcohol **5** in 87% yield, and this was converted into its tosylate **6** (95%). De-



Scheme 1. a) HCO_2Et, NaH/MeOH, Et_2O, 20 °C; b) TsN_3, $HNEt_2$; c) *hν*, MeOH; d) $LiAlH_4$, Et_2O; e) TsCl, pyridine; f) KO*t*Bu, DMSO



Scheme 2. a) $Ph_3PMe^+Br^-$, KO*t*Bu, Et_2O, 20 °C; b) Na, liquid NH_3, EtOH, Et_2O, −70 to −60 °C

hydrotosylation to the target tricyclic alkene **7** was attempted by slow injection of **6**, dissolved in dimethyl sulfoxide (DMSO), into a solution of KO*t*Bu in the same solvent, maintained at 29 °C and under a pressure of 10^{-3} mbar. Under these reaction conditions, volatile products evaporated as they were formed, and were condensed, together with some solvent, in a receiver kept at liquid nitrogen temperature. After workup and separation by preparative gas chromatography, a hydrocarbon fraction was isolated and shown to consist of a 2.5:1 mixture of 4-methylenebicyclo[3.1.0]hex-2-ene (**8**) and **7**. Because of their very similar retention times, the two hydrocarbons could not be separated. From NMR spectroscopic data and by comparison with an authentic sample,[5b,20] the identity of **8** was established without doubt. The NMR signals of the second component fully agreed with those given below for **7**.

A control experiment excluded the possibility that **8** was a later product of **7**, as it demonstrated that treatment with KO*t*Bu in [D_6]DMSO left **7** unchanged. Most probably, the precursor of **8** was already a bicyclo[3.1.0]hex-2-ene derivative, which could have formed from **6** by a rearrangement catalysed by a trace of an acid that might have remained from the preparation of **6**. The acid-catalysed rearrangement of the parent tricyclo[3.1.0.0^{2,6}]hexane to bicyclo[3.1.0]hex-2-ene is well known.[3a]

2. Synthesis of 7 from 4-(Phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]-hexan-3-one (9)

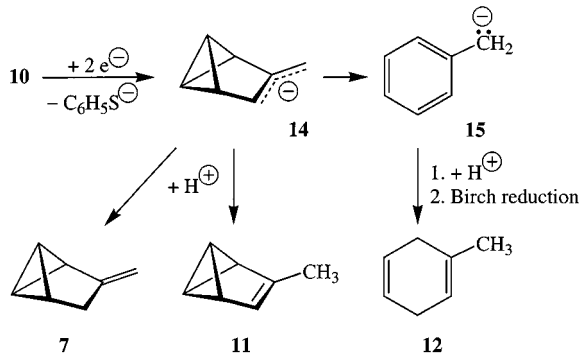
By analogy with the higher homologue,[4] the preparation of **7** should be straightforward from tricyclo[3.1.0.0^{2,6}]-hexan-3-one by means of a Wittig reaction. However, access to this ketone is difficult.[21] On the other hand, a simple synthesis of its 4-phenylsulfanyl derivative **9**, in three steps from benzvalene in an overall yield of 23 %, has recently been discovered.[22] This ketone could be converted into the target **7** in two steps (Scheme 2).

Through a Wittig reaction, we obtained a 56% yield of the phenylsulfanyl derivative **10** of **7**, and this was desulfurised by sodium in liquid ammonia. To achieve an acceptable yield of **7** (24%), we had to add ethanol to the reduction mixture. In the absence of ethanol, the major product was 1-methylcyclohexa-1,4-diene (**12**), in addition to which some **7** and toluene (**13**) were also formed. The presence of ethanol gave rise to a 14:2:1:1 mixture of **7**, **12**, 3-methylbenzvalene (**11**), and **13**. With the aid of NMR spectroscopic data available in the literature, the identification of **11**[23] and **12**[24] was straightforward. The NMR signals of **7** were also highly characteristic. In particular, the ^{13}C NMR spectrum indicated the presence of a bicyclo[1.1.0]butane system by a signal at $\delta = 7.0$, and that of a 1,1-dialkylated ethene moiety by absorptions at $\delta = 99.9$ and 154.2.

Since **11** completely rearranged to **13** at room temperature within 1 d, we do not view the latter as a primary product of the desulfurisation of **10**, the mechanism of which is summarised in Scheme 3. Probably, **10** is transformed in several steps into the allyl anion **14** by incorporation of two electrons and expulsion of a benzenethiolate ion. On protonation of the allyl termini of **14**, mainly the desired product **7** arises, accompanied by some **11**. However, these steps are relatively slow if ammonia is the proton source, providing **14** with the opportunity to rearrange primarily to the benzyl anion (**15**). The protonation of **15** and the Birch reduction of the resulting **13** explain the formation of **12** as main product. Obviously, addition of ethanol to the reaction mixture causes a faster protonation of **14**, and hence increased yields of **7** and **11**. The isomerisation of **14** to **15**, which proceeds rather rapidly even at temperatures of about −60 °C, is considerably faster than that of benzvalene to benzene or that of **11** to **13**.[23]

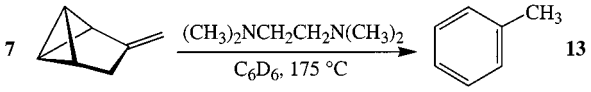
3. Reactions of 7: Thermolysis in Solution and Addition onto TCNE

In order to test the thermal stability of **7**, we heated a C_6D_6 solution of it, which had been prepared carefully to avoid catalysed processes.[3b] At 175 °C, the half-life was found to be about 200 min, with toluene (**13**) as the only product (Scheme 4). Thus, the rearrangement of **7** proceeded considerably more rapidly than that of the parent



Scheme 3

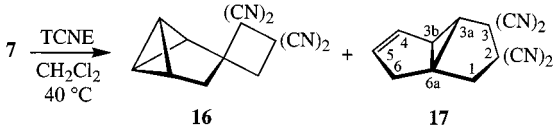
hydrocarbon (tricyclo[3.1.0.0^{2,6}]hexane), which has a similar half-life only at 240 °C.[3a] Possible mechanisms of these isomerisations are discussed in a forthcoming article.[5a]



Scheme 4

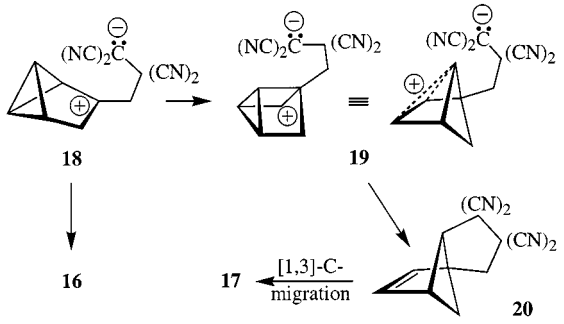
Tetracyanoethylene (TCNE) interacts in various ways with bicyclo[1.1.0]butane[25] and a number of its derivatives.[6,25−28] In the cases of benzvalene[26] and homobenzvalene,[27] a homo Diels−Alder reaction, considered to occur concertedly, onto a vinylcyclopropane subunit takes place (among other processes). Although **7** possesses a vinylcyclopropane moiety, such a reaction appeared unlikely, since the product would be a derivative of (*E*)-cycloheptene.

Warming of a solution of **7** and TCNE in dichloromethane at 40 °C gave rise to a 1:5 mixture of the [2+2] cycloadduct **16** and the cyclopropadicyclopentene derivative **17** (Scheme 5). These products were identified by their NMR spectra. The ^{13}C NMR signals at δ = 6.2 and 6.5 were characteristic for the tricyclo[3.1.0.0^{2,6}]hexane subunit of **16**, while the structure **17** was supported by the presence of an CH=CH−CH$_2$ grouping as part of a cyclopentene moiety, as deduced from the magnitude of the vicinal coupling between the olefinic protons ($J_{4,5}$ = 5.8 Hz) and their interactions with the protons of the methylene group.



Scheme 5

A pentamethyl derivative of **17** has been obtained from a pentamethyl derivative of **7** and TCNE. The mechanism proposed by the authors[6] should be applicable here as well (Scheme 6). Thus, addition of TCNE to the olefinic methylene group of **7** should initially furnish the zwitterion **18**, which can undergo two reactions: either a collapse to give **16**, the minor product, or a Wagner−Meerwein rearrangement in the cationic part with formation of the new zwitterion **19**. This species is represented by a classical and by a nonclassical formula in Scheme 6. The ring-closure of **19**, combining the nucleophile with the electrophilic centre of the one-carbon bridge of the nonclassical structure, generates the bicyclo[2.1.1]hexene derivative **20**, which is subject to a sigmatropic reorganisation resulting in **17**. Hogeveen et al.[6] observed the pentamethyl derivative of **20** directly and determined kinetic data for its conversion into the final product.



Scheme 6

Experimental Section

General: NMR: Varian A 60 D, Varian NV 14, Bruker AM 400, Bruker AC 200, Bruker AC 250; internal standards TMS, $CHCl_3$ (δ = 7.26) and C_6D_5H (δ = 7.15) for ^{1}H NMR and $CDCl_3$ (δ = 77.0) and C_6D_6 (δ = 128.0) for ^{13}C NMR. IR: Perkin−Elmer 257 and 325 infrared spectrometers. UV: Varian Cary 17. MS: Varian MAT CH5 and CH7, Finnigan MAT 8200. Analytical GC (AGC): Perkin−Elmer F-20 and F-22, FID, carrier gas N_2, glass capillary columns; integration with Perkin−Elmer Minigrator M-2 or Hewlett−Packard model 3370/18. Preparative GC (PGC): Varian 90-P and 920, thermal conductivity detector, carrier gas He, glass columns. Elemental analyses: LECO CHNS 932. All experiments described below were conducted in anhydrous solvents in dry glassware and under dry argon or nitrogen.

4-[(*Z*)-Hydroxymethylene]tricyclo[4.1.0.0^{2,7}]heptan-3-one (2) (3-Oxotricyclo[4.1.0.0^{2,7}]heptane-4-carbaldehyde): Sodium hydride (1.08 g of a 55% suspension in mineral oil, 25 mmol NaH) was purified by treatment with pentane and decantation of the liquid phase (3 × 5 mL). Traces of the solvent were removed at room temperature in vacuo, and diethyl ether (155 mL, from $LiAlH_4$) was added. A solution of tricyclo[4.1.0.0^{2,7}]heptan-3-one (**1**,[16] 1.30 g, 12.0 mmol) and ethyl formate (14.4 g, 194 mmol) in 85 mL of diethyl ether was added with stirring to this suspension. The reaction was started by addition of CH_3OH (0.072 mL, 1.8 mmol) and the mixture was stirred at room temperature for 20 h. Another 0.096 mL of CH_3OH was added during that period. Despite a successful experience with the preparation of an analogous compound from bicyclo[3.2.0]-hept-6-en-2-one,[2d] it was not possible to isolate **2** in pure form under various conditions. The above solution of **2** in diethyl ether, containing some CH_3OH and C_2H_5OH, was therefore used directly for diazotization.

4-Diazotricyclo[4.1.0.0^{2,7}]heptan-3-one (3): *p*-Toluenesulfonyl azide[18] (4.80 g, 24.3 mmol) in diethyl ether and freshly distilled diethylamine (5.2 mL, 50 mmol) were added at 0 °C to the above

solution of **2** in diethyl ether. After having been stirred for 4 h at room temperature, the mixture was worked up by addition of 600 mL of an aqueous buffer solution (Na_2HPO_4/KH_2PO_4, pH = 7), followed by extraction with diethyl ether (3 × 50 mL) and dichloromethane (2 × 50 mL). The dried ($MgSO_4$) organic phases were concentrated in vacuo to yield 5.20 g of crude product containing, as shown by ^{1}H NMR analysis, about 20% of **3**, 20% of *p*-toluenesulfonyl azide, 15% of methyl *p*-toluenesulfonate and 45% of ethyl *p*-toluenesulfonate. Yield: 0.70−1.00 g (43−62% relative to **1**) of **3**. For spectral characterisation a small portion was purified by chromatography on Florisil, with diethyl ether/pentane (1:3) as eluant. IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (s), 2850 (m), 2085 (s, C=N$_2$), 1635 (s, C=O), 1260, 1035, 800. ^{1}H NMR (60 MHz, $CDCl_3$): δ = 2.39 (t, $J_{1,2} = J_{1,6} = J_{2,7} = J_{6,7}$ = 2.2 Hz, 2 H, 1-H, 7-H), 2.65−3.00 (m, 4 H, 2-H, 5-H$_2$, 6-H).

Methyl Tricyclo[3.1.0.0^{2,6}]hexane-3-carboxylate (4): A solution of 4-diazotricyclo[4.1.0.0^{2,7}]heptan-3-one (**3**, 0.40 g, 3.0 mmol) in 50 mL of absolute CH_3OH was purged with dry argon and then irradiated (Pyrex, Philips−HPK, 125 W) at room temperature for about 90 min, resulting in evolution of nitrogen (45 mL, corresponding to a yield of 62%). The solvent was carefully removed in vacuo, and the residue was subjected to a short-path distillation at 10^{-3} mbar to yield **4** as a colourless oil of about 90% purity. MS (EI, 70 eV): *m*/*z* (%) = 138 (16) [M$^+$], 107 (37) [$C_7H_7O^+$], 78 (100) [$C_6H_6^+$], 77 (100) [$C_6H_5^+$]. IR: $\tilde{\nu}$ = 3045 cm^{-1} (w), 2950 (m), 2875 (w), 1725 (vs, C=O), 1435, 1195, 1170, 760. ^{1}H NMR (60 MHz, CCl_4): δ = 1.4−2.7 (complex, 7 H, 1-H, 2-H, 3-H, 4-H$_2$, 5-H, 6-H), 3.53 (s, 3 H, CH_3).

(Tricyclo[3.1.0.0^{2,6}]hex-3-yl)methanol (5): Methyl tricyclo[3.1.0.0^{2,6}]hexane-3-carboxylate (**4**, 130 mg, 0.94 mmol) in 0.5 mL of diethyl ether was added to a suspension of $LiAlH_4$ (38 mg, 1.0 mmol) in diethyl ether (4 mL, from $LiAlH_4$). After having been stirred for 18 h at room temperature, the mixture was cooled to 0 °C and then treated with 0.1 mL of H_2O. Filtration of the mixture, drying of the filtrate (Na_2SO_4) and evaporation of the solvent in vacuo yielded **5** (90 mg, 87%) as an oily liquid. MS (EI, 70 eV): *m*/*z* (%) = 110 (9) [M$^+$], 79 (83) [$C_6H_7^+$], 42 (100). IR (film): $\tilde{\nu}$ = 3600−3000 cm^{-1} (s, OH), 3035 (w), 2930 (s), 2865 (s), 1110, 1035, 750. ^{1}H NMR (60 MHz, $CDCl_3$): δ = 1.0−2.4 (complex, 8 H, 1-H, 2-H, 3-H, 4-H$_2$, 5-H, 6-H, -OH), 3.4 (m, 2 H, C*H*$_2$OH).

(Tricyclo[3.1.0.0^{2,6}]hex-3-yl)methyl *p*-Toluenesulfonate (6): At 0 °C, *p*-toluenesulfonyl chloride (137 mg, 0.72 mmol) was added with stirring to tricyclo[3.1.0.0^{2,6}]hex-3-ylmethanol (**5**) (40 mg, 0.36 mmol) in 0.5 mL of pyridine. This solution was kept in the refrigerator for 14 h and then poured into ice/water. The mixture was extracted with diethyl ether. The ether layer was washed with an aqueous buffer solution (pH = 7, 3 × 1 mL) and dried (Na_2SO_4). Removal of the solvent in vacuo at 0 °C gave **6** (90 mg, 95%) as a slightly yellow oil, which was used directly for the elimination reaction. IR (film): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2940 (m), 2865 (w), 1598 (m, arom. C=C), 1495 (w, arom. C=C), 1360, 1190, 1175, 960, 662. ^{1}H NMR (60 MHz, CCl_4): δ = 1.20−2.15 (complex, 7 H, 1-H, 2-H, 3-H, 4-H$_2$, 5-H, 6-H), 2.42 (s, 3 H, CH_3), 3.60−3.83 (m, 2 H, CH_2O), 7.33 (2 H) and 7.73 (2 H) (AA′BB′ spectrum, C_6H_4).

Treatment of 6 with KO*t*Bu − Formation of 3-Methylenetricyclo[3.1.0.0^{2,6}]hexane (7) and 4-Methylenebicyclo[3.1.0]hex-2-ene (8): KO*t*Bu (0.71 g, 6.3 mmol) and dimethyl sulfoxide (10 mL, from CaH_2) were placed in a three-necked flask equipped with a septum and connected through a short-path distillation apparatus to two consecutive traps. After having been purged with argon, the system was slowly evacuated to about 10^{-3} mbar. The reaction flask was immersed in a water bath (29 °C) and, with stirring, a solution of **6** (0.175 g, 0.66 mmol) in dimethyl sulfoxide (1 mL) was slowly injected. Volatile products were condensed in the traps, which were maintained at liquid nitrogen temperature. Stirring was continued for 30 min, and the reaction flask was then warmed to about 50−60 °C, whereupon some DMSO distilled. Water was added to the products in the traps, and the combined mixtures were extracted with pentane (3 × 2 mL). The combined pentane layers were washed with water, dried ($MgSO_4$), and carefully concentrated. The residue was shown by AGC (column: 83.5 m × 0.28 mm, PPG + KOH, 80 °C) to consist of a mixture of **8** (71%, t_R = 15.1 min), **7** (27%, t_R = 15.2 min), toluene (**13**, 2%, t_R = 16.0 min), and some pentane. Separation of this mixture by PGC (column: 2.0 m × 3/8 in, 20% Carbowax 20M + KOH on Chromosorb P 60/80 mesh, 78 °C, 100 mL He/min) gave one fraction (t_R = 11 min) shown by AGC still to be a mixture of **8** (65%) and of **7** (35%), which furnished the following data: GC-MS (EI, 70 eV): *m*/*z* (%) = 92 (100) [M$^+$], 91 (79) [$C_7H_7^+$], 65 (68) [$C_5H_5^+$], 39 (53) [$C_3H_3^+$]. IR (CCl_4): $\tilde{\nu}$ = 3055 cm^{-1} (m), 2995 (w), 1635 (w, C=C), 1620 (w, C=C), 863, 660. UV (cyclohexane): λ_{max} = 245 nm. ^{1}H NMR (60 MHz, CCl_4) for **7**: δ = 4.55 (m), 4.75 (m), and 1.8−2.4 (m) in an intensity ratio of about 1:1:6; further NMR spectroscopic data are given below; for **8**: δ = 0.37 (q, average of $J_{1,6endo}$, $J_{5,6endo}$, and $J_{6endo,6exo}$ = 3.5 Hz, 1 H, 6-H$_{endo}$), 0.95 (td, average of $J_{1,6exo}$ and $J_{5,6exo}$ = 7.5, $J_{6endo,6exo}$ = 3.5 Hz, 1 H, 6-H$_{exo}$), 1.8−2.4 (complex, 2 H, 1-H, 5-H), 4.85 (m, 2 H, =CH$_2$), 5.63 (m) and 6.15 (m) (2 × 1 H, 2-H, 3-H), in agreement with the literature.[20] Independently synthesised sample of **8**:[2d][5b] ^{1}H NMR (400 MHz, $CDCl_3/C_6D_6$): δ = 0.40/0.38 (q, average of $J_{1,6endo}$, $J_{5,6endo}$, and $J_{6endo,6exo}$ = 3.5 Hz, 1 H, 6-H$_{endo}$), 1.02/0.71 (td, average of $J_{1,6exo}$ and $J_{5,6exo}$ = 7.5, $J_{6endo,6exo}$ = 3.5 Hz, 1 H, 6-H$_{exo}$), 2.12−2.21 (m, 2 H, 1-H, 5-H)/1.83 (m, 1 H, 1-H) and 1.96 (m, 1 H, 5-H), 4.91/4.94 (br. s, 1 H, 7-H$_Z$), 5.03/5.05 (br. s, 1 H, 7-H$_E$), 5.77/5.70 (d, $J_{2,3}$ = 5.5 Hz, 1 H, 3-H), 6.28 (dddd, $J_{2,3}$ = 5.5, $J \approx$ 2.5, 1.5, 1.0 Hz)/6.04 (dm) (1 H, 2-H); the assignment is based on H,H COSY spectra and NOE measurements. ^{13}C NMR (101 MHz, $CDCl_3/C_6D_6$): δ = 21.3/21.8 (C-5), 24.1/24.2 (C-6), 24.3/24.7 (C-1), 105.3/105.6 (=CH$_2$), 129.7/130.2 (C-3), 141.4/141.3 (C-2), 154.8/155.0 (C-4); the assignment is based on C,H COSY spectra.

4-Methylenetricyclo[3.1.0.0^{2,6}]hex-3-yl Phenyl Sulfide (10): A mixture of methyltriphenylphosphonium bromide (9.83 g, 27.5 mmol) and freshly sublimed potassium *tert*-butoxide (3.08 g, 27.5 mmol) in diethyl ether (550 mL) was stirred at room temperature for 30 min. The resulting solution was added dropwise to a solution of 4-(phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexan-3-one[22] (**9**, 5.56 g, 27.5 mmol) in diethyl ether (440 mL). Stirring was continued for 3 h at room temperature. The mixture was then diluted with light petroleum ether (b.p. 30−50 °C) (LP) and filtered through basic Al_2O_3 (activity IV) with LP as eluant. After concentration of the filtrate in vacuo, the residue was subjected to flash chromatography (basic Al_2O_3, activity III, LP) to give **10** (3.09 g, 56%) as a yellowish liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.38 (dm, $J_{2,5}$ = 4.9 Hz, 1 H) and 2.49 (m, 1 H) (2-H, 5-H), 2.49−2.53 (m, 2 H, 1-H, 6-H), 3.85 (m, 1 H, 3-H), 4.97 (d, *J* = 1.5 Hz, 1 H) and 5.08 (m, 1 H) (=CH$_2$), 7.21 (tt, 1 H, *p*-H), 7.28 (m, 2 H, *m*-H), 7.43 (m, 2 H, *o*-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.5 and 9.8 (C-1, C-6), 38.0 and 39.4 (C-2, C-5), 50.1 (C-3), 103.7 (=CH$_2$), 126.3 (*p*-C), 128.7 (*m*-C), 130.7 (*o*-C), 136.0 (*i*-C), 153.3 (C-4); the assignment is based on a C,H COSY spectrum. $C_{13}H_{12}S$ (200.3): calcd. C 77.95, H 6.04, S 16.01; found C 77.69, H 6.62, S 15.30.

Reduction of 10 with Sodium in Liquid Ammonia − Formation of 3-Methylenetricyclo[3.1.0.0^{2,6}]hexane (7)

a) In the Absence of Ethanol: A solution of **10** (2.00 g, 9.99 mmol) in diethyl ether (7 mL) was added dropwise to a stirred solution of sodium (949 mg, 41.2 mmol) in liquid ammonia (30 mL), kept at −70 °C. Stirring was continued for 2 h at −60 °C, whereupon NH_4Cl (2.21 g, 41.3 mmol) was carefully added in small portions. The mixture was then allowed to warm to room temperature and the evaporating ammonia was piped through a cold trap (−25 °C) to collect coevaporated product. The residue in the reaction vessel and the contents of the trap were treated with pentane and cold water (0 °C), and the mixtures were combined. After separation of the layers, the aqueous phase was extracted with pentane (4 × 50 mL). The combined pentane layers were dried with Na_2SO_4/K_2CO_3 and concentrated by distillation at 60 °C (bath)/atmospheric pressure through Vigreux columns of 22 cm (initially) and 8 cm length and finally without a column at room temperature/500−600 mbar. Volatile components of the residue were evaporated at 12 mbar in two stages and were condensed in traps cooled with liquid nitrogen. Evaporation at room temperature gave 1.04 g of a colourless liquid consisting of pentane, 1-methylcyclohexa-1,4-diene (**12**), **7**, and toluene (**13**) in a ratio of 10:4:2:1 as analysed by ^{1}H NMR spectroscopy. The signals of **12** were identified from literature data.[24] Evaporation with warming of the residue to 40 °C furnished 186 mg of a colourless liquid shown to be an 8:2:1 mixture of **12**, **7**, and **13**.

b) In the Presence of Ethanol: Liquid ammonia (100 mL) was stirred at −70 °C, and ethanol (12.9 mL), a solution of **10** (923 mg, 4.61 mmol) in diethyl ether (50 mL) and, finally, sodium (802 mg, 34.9 mmol) were added in small portions. After this mixture had been further stirred for 2 h at −60 °C, NH_4Cl (1.89 g, 35.3 mmol) was carefully added in small portions. The mixture was then stirred for a further 30 min at −60 °C and afterwards worked up as in procedure a). Only one product fraction (145 mg of a yellow liquid) was collected by evaporation at 12 mbar and condensation in a cold trap. It consisted mainly of **7**, **12**, 3-methylbenzvalene (**11**), and **13** in a ratio of 14:2:1:1 and some pentane as analysed by ^{1}H NMR spectroscopy immediately after preparation and workup. When the NMR sample ($CDCl_3$) was kept at room temperature for 1 d, **11** converted completely into **13**. The known data for **11**[23] allowed its straightforward identification. Through the use of mesitylene as internal standard, the yield of **7** was determined to be 103 mg (24%). The purification of **7** by gas chromatography is described in a forthcoming paper.[5] ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95 (m, 2 H, 4-H_2), 2.10 (dtq, $J_{2,5}$ = 4.9, $J_{1,5}$ = $J_{5,6}$ = 1.8, J = 0.9 Hz, 1 H, 5-H), 2.27 ("quint", line distance 1.6 Hz, 2 H, 1-H, 6-H), 2.40 (br. dt, $J_{2,5}$ = 4.9, $J_{1,2}$ = $J_{2,6}$ = 1.8 Hz, 1 H, 2-H), 4.69 (m, 1 H) and 4.91 (m, 1 H) (=CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 7.0 (C-1, C-6), 31.9 (C-5), 32.6 (C-4), 40.5 (C-2), 99.9 (=CH_2), 154.2 (C-3); the assignment is based on a C,H COSY spectrum.

Thermolysis of 7 in C_6D_6: $LiAlH_4$ (ca. 20 mg) was added to a solution of one drop of tetramethylethylenediamine, **7** (ca.10 mg, contaminated by some **12** and **13**), and mesitylene (8 mg) in C_6D_6 (0.6 mL). The mixture was kept at 20 °C for 1 h. The volatile components were then evaporated at $2\cdot10^{-5}$ mbar and condensed in an NMR tube, cooled with liquid nitrogen. (Prior to that operation, the evacuated NMR tube had been flame-dried.) While the sample in the NMR tube was still cooled with liquid nitrogen, the NMR tube was evacuated and sealed. As shown by NMR analysis, **7** rearranged cleanly to **13** on heating at 175 °C. From the integrated intensities of **7**, **13**, and mesitylene, the half-life was determined to be ca. 200 min.

Reaction between 7 and Tetracyanoethylene − Formation of Spiro-[cyclobutane-1,3′-tricyclo[3.1.0.0^{2,6}]hexane]-2,2,3,3-tetracarbonitrile (16) and (3a*S,3b*S**,6a*R**)-3b,6-Dihydrocyclopropa[1,2:1,3]dicyclopentene-2,2,3,3(1*H*,3a*H*)-tetracarbonitrile (17):** Tetracyanoethylene (556 mg, 4.34 mmol) was added to a solution of a 4:2:1 mixture of **12**, **7**, and **13**, containing ca. 50 mg (0.54 mmol) of **7**, in dichloromethane (10 mL) at room temperature. The resulting suspension was stirred at 40 °C for 18 h. The solid was then removed by filtration and the filtrate was concentrated in vacuo. Purification of the remaining oil by flash chromatography on silica gel, with a gradient of 11% to 20% to 33% of ethyl acetate in light petroleum ether (b. p. 30−50 °C), gave 51 mg (43%) of a beige solid, shown by NMR to consist of **16** and **17** in the ratio of 1:5. MS (EI, 70 eV): *m*/*z* (%) = 220 (0.7) [M^+], 142 (17), 115 (21), 92 (32), 91 (100), 51 (11), 39 (17). $C_{13}H_8N_4$ (220.2): calcd. C 70.90, H 3.66, N 25.44; found C 70.73, H 3.44, N 25.12.

Compound 16: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.82 (dm, $J_{4',4'}$ = 13.0 Hz, 1 H) and 2.23 (dm, $J_{4',4'}$ = 13.0 Hz, 1 H) (4′-H_2), 2.20 (m, 1 H; 5′-H), 2.42 (dm, $J_{1',6'}$ = 8.9 Hz, 1 H) and 2.50 (dm, $J_{1',6'}$ = 8.9 Hz, 1 H) (1′-H, 6′-H), 2.67 (dt, $J_{2',5'}$ = 5.2, $J_{1',2'}$ = $J_{2',6'}$ = 1.8 Hz, 1 H, 2′-H), 3.04 (s, 2 H, 4-H_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 6.2 and 6.5 (C-1′, C-6′), 32.5 (C-5′), 41.3 (C-4), 41.8 (C-2′), 42.4 (C-4′), 108.8, 110.7, and 111.0 (3 × CN); the signals of the fourth CN group, C-1 (C-3′), C-2, and C-3 were not observed, due either to too low intensity or to being superimposed by signals of **17**; the assignment is based on a C,H COSY spectrum.

Compound 17: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.76 (br. d, $J_{3a,3b}$ = 1.5 Hz, 1 H, 3a-H), 2.75−2.80 (m, 2 H, 6-H_2), 2.86 (m, 1 H, 3b-H), 3.08 (d, $J_{1,1}$ = 14.0 Hz, 1 H) and 3.18 (d, $J_{1,1}$ = 14.0 Hz, 1 H) (1-H_2), 5.77 (dt, $J_{4,5}$ = 5.8, average of 2 $J_{4,6}$ = 2.1 Hz, 1 H, 4-H), 5.92 (dqd, $J_{4,5}$ = 5.8, average of $J_{3b,5}$ and 2 $J_{5,6}$ = 2.1, J = 0.9 Hz, 1 H, 5-H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 32.5 (C-3b), 36.4 (C-3a), 36.9 (C-6), 37.2 (C-6a), 39.2 (C-1), 45.6 (C-2), 55.1 (C-3), 109.9, 110.2, 110.3 111.4 (4 × CN), 130.4 (C-5), 132.3 (C-4); the assignment is based on a C,H COSY spectrum.

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