1,2,3,5-Tetrahydro-1,2,3-methenopentalene, a Valence Isomer of Isoindene: Synthesis and Diels–Alder Reactions[**]

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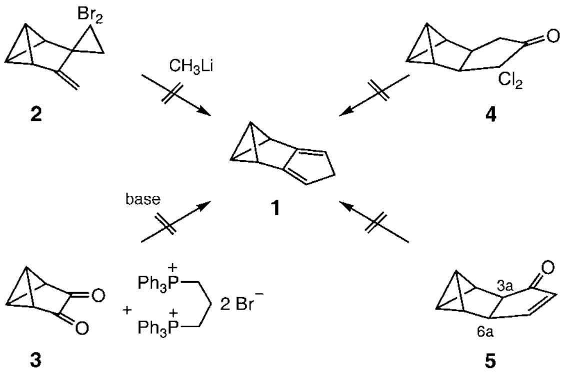
Dedicated to Professor Waldemar Adam
on the occasion of his 65th birthday

The fascinating chemistry of isodicyclopentadiene, explored by Bartlett et al.[1] and Paquette et al.,[2] provoked our interest in the title compound **1**. Its Diels–Alder reactions were expected to furnish benzvalene derivatives with a substantially pyramidalized double bond, which should give rise to interesting properties. Our attempts to prepare **1** following established methods for the synthesis of cyclopentadienes failed without exception (Scheme 1). Thus, the treatment of the 1,1-dibromo-2-vinylcyclopropane **2** with methyllithium resulted in the formation of the corresponding allene rather than giving **1** in a Skattebøl rearrangement.[3] By using various bases, the α-diketone **3**[4] and propanediyl(triphenylphosphonium) dibromide could not be transformed to **1**.[5] A number of conceivable routes to **1** starting from the dichlorocyclopentanone **4**[3] and from the cyclopentenone **5**[6] proved impassable,[7,8] although both already consist of the carbon skeleton of **1**.



Scheme 1. Attempted but unsuccessful routes to the title compound **1**.

In the case of the reaction sequences using **5**, invariably "escape reactions" occurred whenever a proton had to be removed from the bridgehead position 3a or 6a with regard to the formation of **1**. These findings made us look for a starting material containing a functional group that could be removed in a different way than a proton in the decisive stage. 3-(Phenylsulfanyl)benzvalene (**6**) was chosen, which is readily accessible from benzvalene in two steps.[9] The Pauson–Khand reaction of **6** could be performed in yields (36–41 %) similar to those of the reaction of unsubstituted benzvalene[6] and gave rise to the regioisomeric (phenylsulfanyl)cyclopentenones **7a** (Table 1) and **7b** in a ratio of 10:1 (Scheme 2).

Both isomers **7** could be converted into the target compound **1** in four steps. The allylic alcohols formed on reduction

Table 1. Selected physical and spectroscopic data of compounds **1**, **7a**, **11**, **12**, and **16**.[a]

1: M.p. 29–32 °C; ^{1}H NMR (200 MHz): $\delta = 2.56$ (t, $J = 1.7$ Hz, 2H; H1,3), 3.32 (pseudo-quint, line distance 1.8 Hz, 2H; H2,7), 3.38 (pseudo-quint, line distance 1.7 Hz, 2H; 2 H5), 5.53 ppm (br. t, $J = 1.4$ Hz, 2H; H4,6); ^{13}C NMR (101 MHz): $\delta = 22.3$ (dq, $J_{\mathrm{C,H}} = 219$, 5 Hz; C2,7), 32.2 (br. dd, $J_{\mathrm{C,H}} = 172$, 10 Hz; C1,3), 48.8 (tt, $J_{\mathrm{C,H}} = 126$, 9 Hz; C5), 112.6 (dq, $J_{\mathrm{C,H}} = 169$, 5 Hz; C4,6), 156.1 ppm (m; C3a,6a); MS (EI, 70 eV): m/z (%): 116 (59) [M^+], 115 (100), 89 (11), 63 (7), 58 (8).

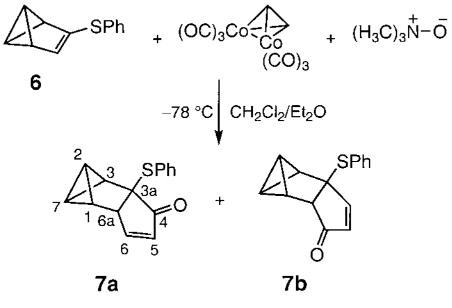
7a: ^{1}H NMR (200 MHz): $\delta = 2.13$ (dq, $J = 8.7$, 1.6 Hz, 1H; H7), 2.22–2.25 (m, 2H; H1,3), 2.42 (dt, $J = 8.7$, 1.6 Hz, 1H; H2), 3.09 (m, 1H; H6a), 5.91 (dm, $J = 6.0$, 1H; H5), 7.18–7.34 (m, 4H; H3,5 and H4 of C_6H_5, H6), 7.50 ppm (m, 2H; H2,6 of C_6H_5); ^{13}C NMR (50 MHz): $\delta = 3.3$ (C7), 12.0 (C2), 36.9 and 39.4 (C1,3), 57.3 (C6a), 65.5 (C3a), 128.2 (C4 of C_6H_5), 128.3 (C3,5 of C_6H_5), 131.0 (C1 of C_6H_5), 133.0 (C5), 135.2 (C2,6 of C_6H_5), 161.8 (C6), 205.6 ppm (C4); IR (film): $\tilde{\nu} = 1710$ cm^{-1}.

11: ^{1}H NMR (600 MHz, −40 °C): $\delta = 2.11$ (dt, $J = 11.4$, 1.5 Hz, 1H) and 2.18 (dt, $J = 11.4$, 1.5 Hz, 1H) (2 H9), 2.39 (≈t, $J = 1.4$ Hz, 1H; H1,3), 4.22 (t, $J = 1.5$ Hz, 1H; H4,7), 4.38 (dt, $J = 10.1$, 1.8 Hz, 1H; H2), 4.70 (dt, $J = 10.1$, 1.0 Hz, 1H; H8); ^{13}C NMR (151 MHz, −40 °C): see Scheme 6.

12: ^{1}H NMR (400 MHz): $\delta = 2.69$ (dt, $J = 3.9$, 1.8 Hz, 1H) and 2.81 (dtd, $J = 3.9$, 1.9, 0.6 Hz, 1H) (H5,7), 3.07 (dt, $J = 8.0$, 1.8 Hz, 1H) and 3.16 (br. d, $J = 8.0$ Hz, 1H) (H6,8), 3.28 (ddd, $J = 19.3$, 10.9, 3.2 Hz, 1H) and 3.45 (ddt, $J = 19.3$, 4.3, 1.0 Hz, 1H) (2 H3), 3.43 (dd, $J = 10.9$, 4.3 Hz, 1H; H2a), 5.75 ppm (m, 1H; H4); ^{13}C NMR (151 MHz): $\delta = 14.2$ (d, ${}^{1}J_{\mathrm{C,H}} = 226$ Hz) and 15.3 (d, ${}^{1}J_{\mathrm{C,H}} = 224$ Hz) (C6,8), 32.7 (d, ${}^{1}J_{\mathrm{C,H}} = 177$ Hz) and 37.0 (d, ${}^{1}J_{\mathrm{C,H}} = 176$ Hz) (C5,7), 45.2 (t, ${}^{1}J_{\mathrm{C,H}} = 133$ Hz; C3), 48.0 (d, ${}^{1}J_{\mathrm{C,H}} = 157$ Hz; C2a), 53.4 (s) and 57.8 (s) (C1,2), 73.3 (s; C7a), 109.12 (s), 109.14 (s), 109.4 (s), and 111.5 (s) (4 CN), 122.0 (d, ${}^{1}J_{\mathrm{C,H}} = 170$ Hz; C4), 154.1 ppm (s; C4a).

16: ^{1}H NMR (600 MHz, −40 °C): $\delta = 2.69$ (dt, $J = 9.1$, 4.0 Hz, 1H) and 2.87 (dt, $J = 9.1$, 2.3 Hz, 1H) (H6,11), 2.89 (m, 2H; H5,7), 3.03 (d, $J = 12.6$, 1H) and 3.27 (dt, $J = 12.6$, 8.9 Hz, 1H) (2 H10), 4.85 ppm (d, $J = 8.9$, 2H; H3,9); ^{13}C NMR (151 MHz, −40 °C): $\delta = 12.1$ (dm, $J_{\mathrm{C,H}} = 216$ Hz) and 16.6 (dm, $J_{\mathrm{C,H}} = 213$ Hz) (C6,11), 48.5 (ddm, $J_{\mathrm{C,H}} = 155$, 15 Hz; C5,7), 50.3 (t, $J_{\mathrm{C,H}} = 142$ Hz; C10), 82.6 (dt, $J_{\mathrm{C,H}} = 156$, 5 Hz; C3,9), 213.4 ppm (d, $J_{\mathrm{C,H}} = 7$ Hz; C4,8).

[a] ^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$ at about 25 °C, if not indicated otherwise; as far as specified, the assignments are based on C,H-COSY spectra.



Scheme 2. Pauson–Khand reaction of **6**.

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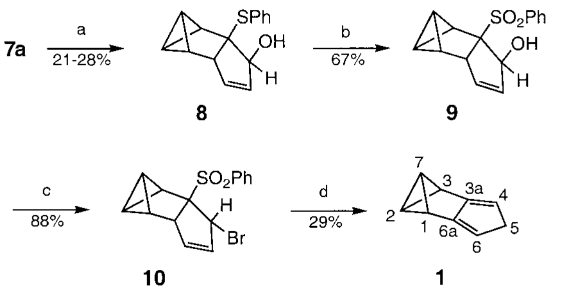
of **7** were oxidized to the sulfones, from which the allyl bromides were prepared by employing the Appel reaction. Finally, the bromine atom and the sulfonyl group were removed by reductive elimination. Scheme 3 illustrates this reaction sequence with the intermediate products **8**–**10**, the isomers of which (two in the case of **8** and **9** and three in the case of **10**) analogously served as precursors of **1**.



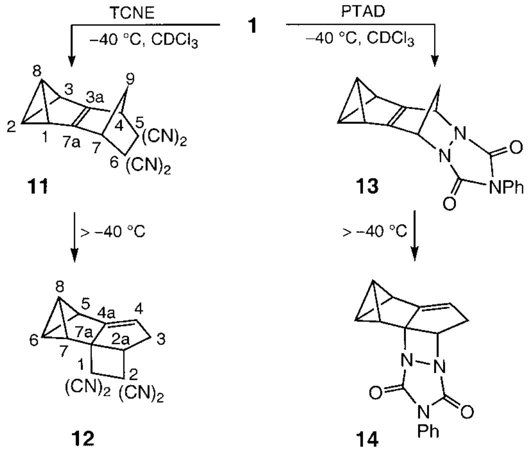
Scheme 3. Synthesis of **1** from **7**. Reagents and conditions: a) diisobutylaluminum hydride, petroleum ether (b.p. 40–65 °C)/dichloromethane 5:1, 0–5 °C; besides **8**, its stereoisomer (34–38 %, from **7a**) and its regioisomer (7–9 %, from **7b**) are formed (yields apply to the total amount of the 10:1 mixture of **7a** and **7b** employed); all isomers have been obtained pure by flash chromatography on SiO_2. b) *m*-Chloroperbenzoic acid, dichloromethane, −20 °C; c) $P(NMe_2)_3$, CBr_4, NEt_3, THF, −20 °C to +20 °C (30 min) and then 60 °C (20 h); besides **10**, its stereoisomer and a regioisomer were formed in small amounts; d) Na/Hg (3 % Na), THF/MeOH 3:1, −20 °C.

Initially, a tautomer of **1** should result from **10** and its isomers. The observation of only **1** characterizes it as the most stable species. The tautomer having a double bond between the bridgehead positions 3a and 6a should be the second intermediate. Burger et al.[10] obtained a small amount of this compound and described it as stable at low temperatures. The ^1H NMR spectrum of **1** shows the pecularity of an interaction through six bonds, which leads to line distances of about 1.8 Hz in the signals of H2, H7, and H5 (Table 1).

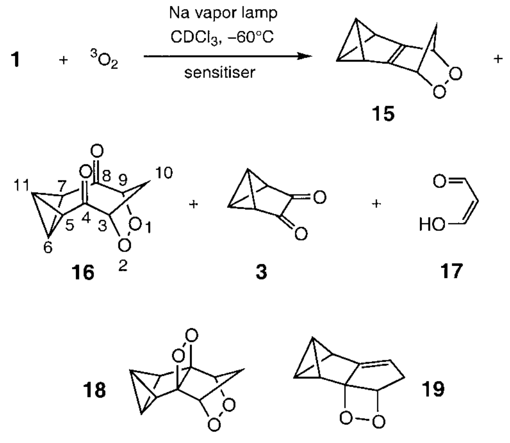
The reactions of **1** with dimethyl acetylenedicarboxylate (20 °C), (*E*)-bis(phenylsulfonyl)ethene (20 °C), and 1,2-dehydrobenzene (−40 °C) yielded the aromatized isomers instead of the Diels–Alder adducts. Probably, the benzvalenes were formed initially, but rearranged subsequently, although unsubstituted benzvalene has a half life of 48 h at 30 °C.[11]

When we treated **1** at −40 °C with tetracyanoethene (TCNE) and 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (PTAD), the benzvalenes **11** (Table 1) and **13**, respectively, were observed at low temperature, but on warming up transformed to the formal [2+2] cycloadducts **12** (Table 1) and **14** (Scheme 4), probably via zwitterionic intermediates. Compounds analogous to **12** and **14** have been obtained by the reaction of 1,2,3,5-tetrahydro-1,3-methanopentalene with TCNE and PTAD, without the Diels–Alder adducts having been observed.[12]

The reaction of **1** with an excess of singlet oxygen ($^1O_2$) in $CDCl_3$ at −60 °C gave the dioxoninedione **16** (Table 1), the *α*-diketone **3**, and the *cis*-enol of malondialdehyde (**17**).[13] By using an internal standard the yields of **16**, **3**, and **17** have been determined to be 14, 16, and 11 %, respectively. Use of a smaller amount of oxygen allowed the observation of the Diels–Alder adduct **15** (ratio **15**:**16**:**3**:**17**:**1** = 3.1:2.1:1.5:1.1:1.0) (Scheme 5). During the recording of NMR spectra at −40 °C the product ratio did not change over several hours, but **15** and **16** decomposed unspecifically at higher temperatures.



Scheme 4. Products of the reactions of **1** with TCNE and PTAD.



Scheme 5. Products of the reaction of **1** with $^1O_2$ and possible intermediates en route to **3**, **16**, and **17** (sensitiser = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin).

We assume that **15** reacts with $^1O_2$ to give the 1,2-dioxetane **18**, which, in competing processes, turns into **16** on one hand as well as **3** and **17** on the other. Whilst the transition **18**→**16** corresponds to the standard process of 1,2-dioxetanes,[14] the formation of **3** and malondialdehyde, brought about by the rupture of four bonds, seems to be without precedent. The most closely related process is the generation of succindialdehyde and ethene on flash vacuum thermolysis of 2,3-oxabicyclo[2.2.2]octane, which involves the cleavage of only three bonds.[15] Alternatively, the dioxetane **19** could serve as a precursor to **3** and **17**. To that end, it would have to combine with $^1O_2$ to afford a bis(dioxetane) or to undergo a [2+2] cycloreversion resulting in an *α*,*β*-unsaturated ketone carrying an aldehyde functionality, which would in turn have to yield a further dioxetane on addition of $^1O_2$. The cleavage of these dioxetanes would clearly account for the formation of **3** and **17**, however, neither the reaction of 1,3-dienes with $^1O_2$ to give bis(dioxetanes) nor the addition of $^1O_2$ to *α*,*β*-unsaturated ketones is known.[14] Since **15** does not rearrange to **19** at −40 °C, **19** would have to be generated parallel to **15** and to be subject to a subsequent reaction immediately. We believe this to be highly unlikely, since simple dioxetanes are frequently observable or even isolable,[14] which also applies to the dioxetane accessible from unsubstituted benzvalene.[16]

Lacking direct structural information, we performed a quantum-chemical calculation (UB3LYP/cc-pVDZ)[17] of **20**, the parent hydrocarbon to **11**. The geometry of the energy minimum is shown in Figure 1. In particular, the projection in the direction of the double bond illustrates its pyramidalization, which has a value of 21.2° and thus amounts almost to that of a *syn*-sesquinorbornatriene (22.7°)[2c]

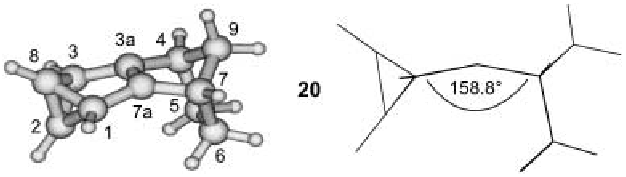
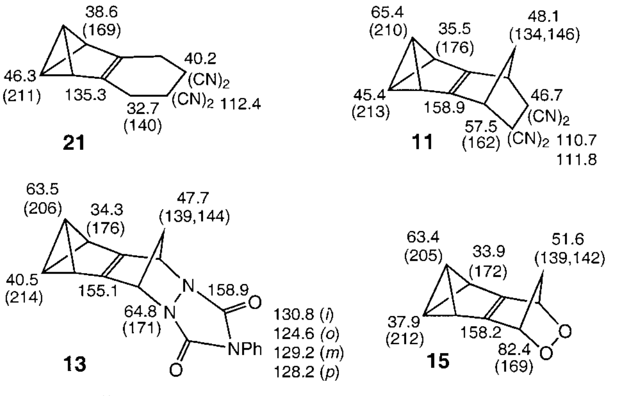


Figure 1. Quantum-chemical calculation of the minimum geometry of 2,3,4,5,6,7-hexahydro-4,7-methano-1,2,3-metheno-1*H*-indene (**20**): perspective view (left) and projection in the direction of the double bond (C3a–7a, right).

As a possible consequence of the pyramidalization, we consider the exceptionally large differences between the chemical shifts of the bicyclobutane bridgehead carbon atoms of **11**, **13**, and **15** (20.0, 23.0, and 25.5 ppm, respectively, Scheme 6). Moreover, the olefinic carbon atoms experience a strong deshielding. The comparison of the data of the ordinary benzvalene **21**[18] with those of **11** emphasizes the unusual character of the benzvalene subunits of **11**, **13**, and **15**.



Scheme 6. ^{13}C chemical shifts and one-bond C,H ncoupling constants (in parentheses) of benzvalene derivatives: CDCl$_3$, −40 °C for **11**, **13**, and **15**; (CD$_3$)$_2$CO, 24 °C for **21**.

In conclusion, a challenging synthetic goal has been achieved by the preparation of the title compound **1.** It is a cyclopentadiene derivative, the Diels–Alder adducts of which are highly reactive and hence observable at best at low temperatures. Further, we anticipate interesting properties for the cyclopentadienyl anion of **1**.

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[18] F. Lanzendörfer, M. Christl, *Angew. Chem.* **1983**, *95*, 896–897; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 871–872; different from the published value (3.0 Hz), the coupling constant between the central and the lateral bicyclo[1.1.0]butane protons of **21** has a value of only 1.5 Hz.