

6,7-Dimethylene-2,4-diphenylbicyclo[3.2.1]oct-3-en-2-yl Anion. A Test for the Origin of the Unusual Properties of the Bicyclo[3.2.1]octa-3,6-dien-2-yl Anion

Manfred Christl,* Roland Leß and Heinrich Müller

Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

On the basis of the ^{13}C NMR spectra of the 6,7-dimethylene-2,4-diphenylbicyclo[3.2.1]oct-3-en-2-yl anion **12**, which has been prepared in four steps from 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene **7**, and the 2,4-diphenylbicyclo[3.2.1]octa-3,6-dien-2-yl anion **11**, it seems reasonable to ascribe a bishomoaromatic character to **11**.

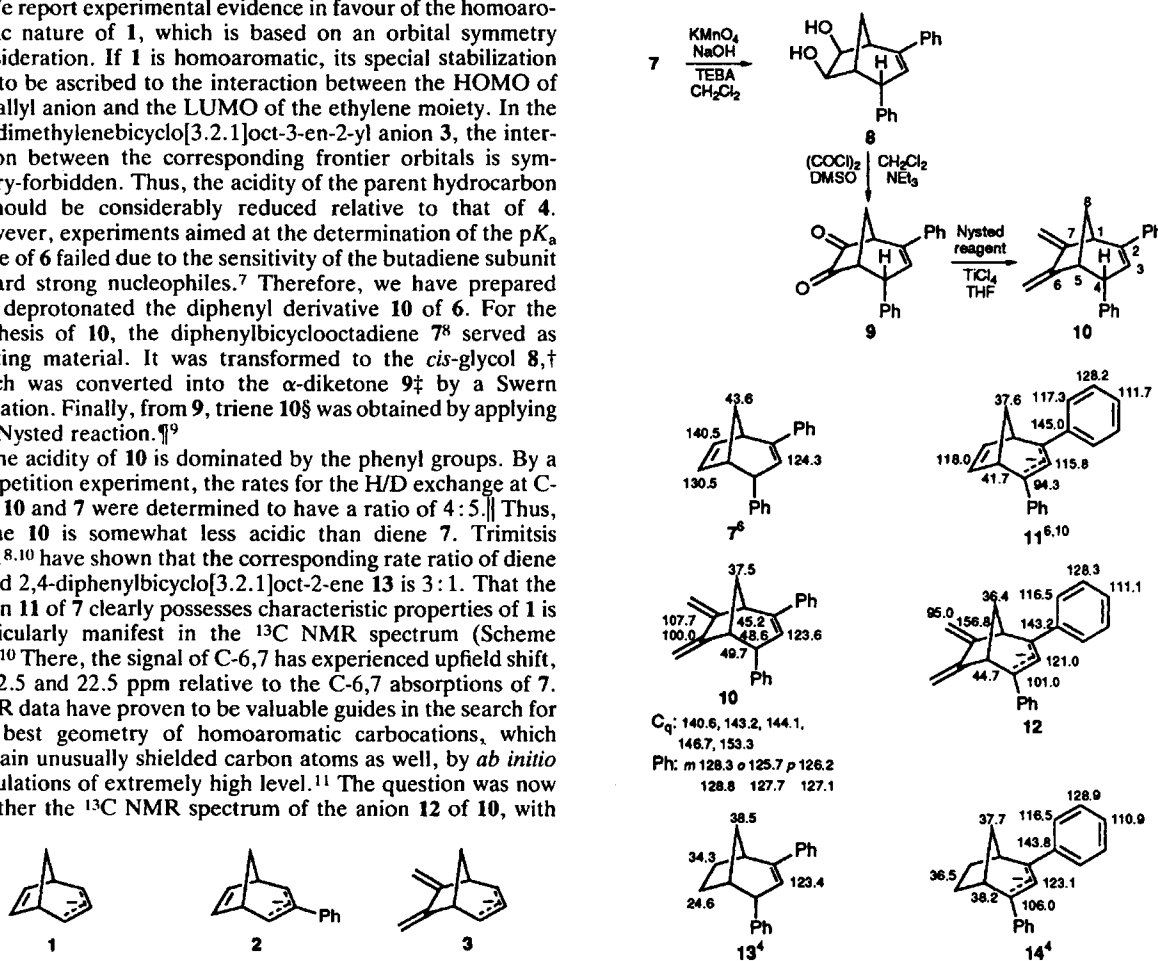
Due the work of Brown and Ocolowitz¹ as well as Winstein *et al.*² the bicyclo[3.2.1]octadienyl anion **1** was regarded as the prototype of anionic homoaromaticity. Although its unusual properties are undisputed, quantumchemical calculations gave no evidence for a homoconjugation between the allyl anion and ethylene moiety.³ In consequence, the peculiarities of **1** have been attributed to an inductive effect, negative hyperconjugation and the interaction with the counter ion.^{3c} By means of the NMR spectra of phenyl-substituted models, it has recently been shown that these effects cannot be of importance.⁴ Being only slightly enhanced relative to that of the parent hydrocarbon **4**, the acidity of 3-phenylbicyclo[3.2.1]octa-2,6-diene **5** was taken as evidence against a homoaromatic stabilization in the corresponding anions **1** and **2**.⁵ That this is not a necessary conclusion has been demonstrated previously on the occasion of the interpretation of the ^{13}C NMR spectrum of **2**.⁶

We report experimental evidence in favour of the homoaromatic nature of **1**, which is based on an orbital symmetry consideration. If **1** is homoaromatic, its special stabilization has to be ascribed to the interaction between the HOMO of the allyl anion and the LUMO of the ethylene moiety. In the 6,7-dimethylenebicyclo[3.2.1]oct-3-en-2-yl anion **3**, the interaction between the corresponding frontier orbitals is symmetry-forbidden. Thus, the acidity of the parent hydrocarbon **6** should be considerably reduced relative to that of **4**. However, experiments aimed at the determination of the $\text{p}K_{\text{a}}$ value of **6** failed due to the sensitivity of the butadiene subunit toward strong nucleophiles.⁷ Therefore, we have prepared and deprotonated the diphenyl derivative **10** of **6**. For the synthesis of **10**, the diphenylbicyclooctadiene **7**⁸ served as starting material. It was transformed to the *cis*-glycol **8**,[†] which was converted into the α -diketone **9**[‡] by a Swern oxidation. Finally, from **9**, triene **10**[§] was obtained by applying the Nysted reaction.⁹

The acidity of **10** is dominated by the phenyl groups. By a competition experiment, the rates for the H/D exchange at C-4 of **10** and **7** were determined to have a ratio of 4:5.^{||} Thus, triene **10** is somewhat less acidic than diene **7**. Trimitsis *et al.*^{8,10} have shown that the corresponding rate ratio of diene **7** and 2,4-diphenylbicyclo[3.2.1]oct-2-ene **13** is 3:1. That the anion **11** of **7** clearly possesses characteristic properties of **1** is particularly manifest in the ^{13}C NMR spectrum (Scheme 1).^{6,10} There, the signal of C-6,7 has experienced upfield shift, of 12.5 and 22.5 ppm relative to the C-6,7 absorptions of **7**. NMR data have proven to be valuable guides in the search for the best geometry of homoaromatic carbocations, which contain unusually shielded carbon atoms as well, by *ab initio* calculations of extremely high level.¹¹ The question was now whether the ^{13}C NMR spectrum of the anion **12** of **10**, with

respect to the diphenylallyl part, is more similar to that of **11** or to that of the diphenylbicyclooctenyl anion **14**. The remarkable difference between **11** and **14** has been discussed previously.⁴

Triene **10** was deprotonated by using methyl lithium in ether, and the NMR spectra of **12** were recorded in $[\text{2H}_8]\text{THF}$.^{**} The ^{13}C NMR spectrum (Scheme 1) reveals that C-2,4 and C-3 are shielded by 6.7 and 5.2 ppm, respectively, relative to these carbon atoms in **11** and deshielded by only 5.0 and 2.1 ppm, respectively, relative to these carbons in **14**. Also, the signals of the phenyl groups display a greater similarity between **12** and **14** than between **12** and **11**. Being smaller than those of **11**, the values of the *o*- and *p*-carbon atoms of **12** indicate somewhat more negative charge in the phenyl groups of **12**. These findings are at variance with the expectations based on inductive effects of and negative



Scheme 1 ^{13}C NMR chemical shifts of the hydrocarbons **7**, **10**, and **13** (CDCl_3 as solvent) and the corresponding allyl anions (Li^+ as counter ion) **11**, **12** ($[\text{2H}_8]\text{THF}$ as solvent and internal reference, $\delta_{\text{C}-2}$ 67.4), and **14** ($[\text{2H}_{10}]\text{DME}$ as solvent and internal reference, $\delta_{\text{C}-1}$ 71.7)

hyperconjugation by C-6 and C-7 as origin of the unusual spectrum of **11**.

Highly interesting is the deprotonation effect on the ^{13}C chemical shifts of the butadiene subunit of **10**. In **12**, the quaternary carbon atoms (C-6,7) are deshielded by at least 3.5 and 10.1 ppm, whereas the methylene carbon atoms have experienced a shielding by 5.0 and 12.7 ppm. These shifts are rationalized by a polarization of the ethylene moieties under the influence of the negative charge, *i.e.* by a move of the electrons toward the methylene group to gain a larger distance from the allyl anion subunit.

Since the deprotonation effects on the butadiene carbon atoms of **10** sum up at best to a small net shielding, the much larger upfield shift of C-6,7 on conversion of **7** into **11** must have a different origin. Direct interactions C-2–C-7 and C-4–C-6 in the sense of a homoaromatic character of **11** offer the simplest explanation. Thereby, the coordination number of these carbon atoms is increased, thus changing their sp^2 hybridization somewhat toward sp^3 .

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Footnotes

† 53% yield; mp 105–107 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 1.64 (br, 2 H, OH), 1.91 (br d, $J_{8,8} = 11.4$ Hz, 8- H_{syn}), 2.41 (ddd, $J_{5,8\text{anti}} = 5.3$, $J_{1,8\text{anti}} = 4.5$ Hz, 8- H_{anti}), 2.46 (\approx tt, $J_{4,5} = 4.3$, $J_{1,5} = J_{3,5} = 1.3$ Hz, 5-H), 3.02 (dd, 1-H), 4.00 (dd, $J_{3,4} = 2.9$ Hz, 4-H), 4.03, 4.22 (2 \times dd, $J_{6,7} = 6.0$, $J_{6,8\text{syn}} = J_{7,8\text{syn}} = 1.2$ Hz, 6-H, 7-H), 6.00 (dd, 3-H), 7.20–7.40 (m, 8 H), 7.50 (m, 2 H) (2 C_6H_5).

‡ 90% yield; mp 123–125 °C; IR (CCl_4) $\tilde{\nu}/\text{cm}^{-1} = 1749$, 1767 (C=O); UV (MeCN) $\lambda_{\text{max}}/\text{nm}$ (log $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 474 (1.987), 310 (sh, 2.759), 248 (4.163), 216 (4.158); $^1\text{H NMR}$ (CDCl_3 , 250 MHz) δ 2.49 (dt, $J_{8,8} = 12.3$, $J_{1,8\text{anti}} = J_{5,8\text{anti}} = 4.7$ Hz, 8- H_{anti}), 2.62 (d, 8- H_{syn}), 3.13 (td, $J_{1,5} = 1.9$ Hz, 5-H), 3.96 (dd, 1-H), 4.28 (dd, $J_{4,5} = 4.9$, $J_{3,4} = 2.6$ Hz, 4-H), 6.35 (d, 3-H), 7.06 (m, 2 H), 7.24–7.44 (m, 6 H), 7.56 (m, 2 H) (2 C_6H_5); this diketone was not stable in CDCl_3 solution and rearranged to an extent of 85% to 2,8-anti-diphenylbicyclo[3.2.1]oct-2-en-6,7-dione within a month at room temperature.

§ 28% yield; colourless oil; MS (70 eV) m/z 284 (8%) [M^+], 220 (28), 206 (16), 205 (100), 189 (10), 177 (11), 168 (10), 167 (27), 165 (11), 91 (11), 81 (12), 57 (34), 41 (12); $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 2.16 (dt, $J_{8,8} = 10.7$, $J_{1,8\text{anti}} = J_{5,8\text{anti}} = 4.6$ Hz, 8- H_{anti}), 2.21 (br d, 8- H_{syn}), 3.01

(br, t, 5-H), 3.59 (br d, 1-H), 4.13 (dd, $J_{4,5} = 4.5$, $J_{3,4} = 2.8$ Hz, 4-H), 3.97, 4.86, 5.15, 5.22 (4 \times br s, 2 $\text{C}=\text{CH}_2$), 5.87 (br d, 3-H), 7.15 (m, 2 H), 7.18–7.42 (m, 6 H), 7.53 (m, 2 H) (2 C_6H_5); correct elemental analysis.

¶ The Nysted reagent⁹ was purchased from Aldrich-Chemie GmbH & Co. KG. Its preparation from zinc and dibromomethane in THF is described in ref 9(a).

|| A 1:1 mixture of **7** and **10** (0.11 mmol each) was dissolved in [$^2\text{H}_6$]DMSO (0.7 ml) and treated with two drops of a solution of sodium (10 mg) in CD_3OD (0.4 ml) at ambient temperature. $^1\text{H NMR}$ spectra taken after 2, 3, 8, 12, and 15 min indicated half-lives of 4 and 5 min for **7** and **10**, respectively.

** The procedure for the preparation of the NMR sample of **12** was that as described for **11** in ref. 6 $^1\text{H NMR}$ of **12** (200 MHz, the H-2 signal of [$^2\text{H}_7$]THF at δ 3.58 served as internal reference) δ 1.69–1.78 (m, 8- H_2), 3.38 (br s, 1,5-H), 4.67, 4.74 (2 \times d, $^2J = 0.8$ Hz, 2 $\text{C}=\text{CH}_2$), 5.89 (tt, $^3J = 6.8$, $^4J = 1.5$ Hz, *p*-H), 6.65 (m, *m*-H), 6.76 (m, *o*-H), 6.96 (s, 3-H).

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