Effect of a 3-Phenyl Substituent on the Acidity of Bicyclo[3.2.1]octa-2,6-diene

George Trimitsis,*[a] John Rimoldi,[a] Milton Trimitsis,[a] James Balog,[a] Fu-Tyan Lin,[b] Alan Marcus,[b] Kasi Somayajula,[b] Samantha Jones,[a] Timothy Hendrickson,[a] and Scott Kincaid[a]

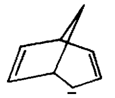
[a] *Department of Chemistry, University of Pittsburgh at Johnstown, Johnstown, PA 15904, U.S.A.*
[b] *Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.*

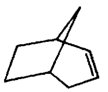
3-Phenylbicyclo-octadiene (**3**) has undergone base-catalysed hydrogen–deuterium exchange at C-4 only slightly faster than the parent hydrocarbon, bicyclo-octadiene (**4**), thereby ruling out the presence of significant homoaromatic stabilization in the bicyclo-octadienyl anion (**1**).

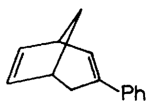
For the past two decades the bicyclo-octadienyl anion (**1**) has been the focal point of the controversy concerning the presence of homoaromaticity in carbanions.[1] In general, experimentally derived data for (**1**) and related anions have been consistent with long range π interactions and homoaromatic stabilization,[2] while nearly all theoretical studies have led to the conclusion that such effects are unlikely.[3,4] Instead, the unusually high stablility of carbanion (**1**) relative to its 6,7-dihydro analogue (**2**) has been attributed to a number of other stabilizing mechanisms including inductive effects, negative hyperconjugation, and gegenion interactions.[3]

We now report the first experimentally derived evidence strongly suggesting that homoaromatic stabilization in carbanion (**1**), if at all present, must be negligibly small. Our conclusions are based on the observation that 3-phenylbicyclo[3.2.1]octa-2,6-diene (**3**) was found to undergo base-catalysed hydrogen–deuterium exchange at C-4 only marginally faster than the unsubstituted hydrocarbon (**4**). The effect of the phenyl group at C-3 is of crucial importance since this position constitutes a node in the HOMO of anion (**1**) if the latter is allylic, but not if this species displays long range π interactions and homoaromaticity[5] [see structure (**5**)].

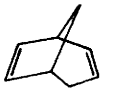
3-Phenylbicyclo-octadiene (**3**) was synthesized from 3-bromobicyclo-octadiene (**7**) as shown in Scheme 1.[6] Thus, treatment of the bromide (**7**)[7] (21.6 mmol) in ether with t-butyl-lithium (43.2 mmol) at −78 °C, gave the organolithium intermediate (**8**) which was subsequently reacted with $ZnCl_2$ (21.6 mmol) in tetrahydrofuran (THF) to give the organozinc reagent (**9**). The latter was added to a mixture of iodobenzene (18.0 mmol) and tetrakis(triphenylphosphene)palladium(0) (0.18 mmol), and stirred for 18 h at room temperature, to afford after acidification and purification (flash chromatography, silica gel 230—400 mesh, light petroleum), the desired product (**3**) in *ca.* 65% yield.† The unsubstituted hydrocarbon (**4**) was also synthesized from the bromide (**7**) in one step, by treatment of the latter with t-butyl-lithium (Scheme 1), followed by an aqueous work-up.‡

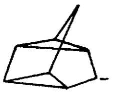

(1)

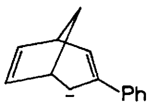

(2)



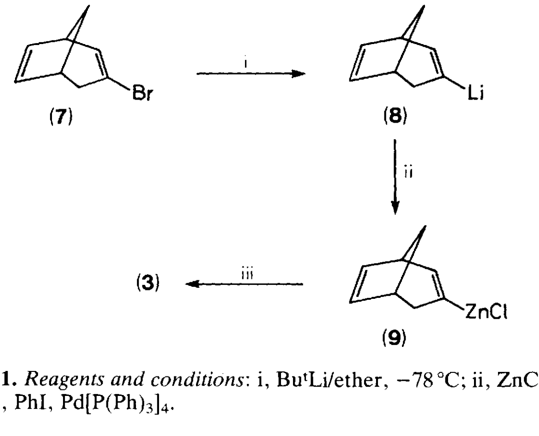
(3)


(4)


(5)



(6)



Scheme 1. *Reagents and conditions*: i, Bu^{t}Li/ether, −78 °C; ii, $ZnCl_2$, THF; iii, PhI, $Pd[P(Ph)_3]_4$.

Next, the rate of the base-catalysed hydrogen–deuterium exchange of 3-phenylbicyclo-octadiene (**3**), relative to bicyclo-octadiene (**4**) was examined. The exchange experiments were carried out in perdeuteriated dimethyl sulphoxide ([$^2H_6$]DMSO) at 60.0 °C with potassium t-butoxide as the base. These conditions were chosen so that the exchange rate of (**4**) can be compared with that reported earlier by Brown and Occolowitz.[2g] In a typical run, a mixture consisting of dienes (**3**) and (**4**) (11.8 mmol each) was added to a solution of potassium t-butoxide (0.024 M, 36 ml) in [$^2H_6$]DMSO maintained at 60.0 ± 0.1 °C, and aliquots were withdrawn at regular intervals over a period of *ca.* 1 h. The aliquots were quenched in aqueous HCl, and subsequently extracted with pentane. Removal of the solvent gave the partially deuteriated dienes (**3**) and (**4**), and the extent of deuterium incorporation was determined by low voltage mass spectrometry (*ca.* 10 eV). The pseudo first-order rate constants (k_1) of hydrocarbons (**3**) and (**4**) were determined by plotting the log of the undeuteriated hydrocarbons *vs.* time (log d_0 *vs.* t),[2g,5] while their

Table 1. Rate constants for hydrocarbons (**3**) and (**4**).

Hydrocarbon	k_1/s^{-1}	$k_2/mol^{-1}\,dm^3\,s^{-1}$	Ratio (3) : (4)
(3)	4.3×10^{-4}[a]	1.8×10^{-2}[c]	4.8[c,e]
(4)	9.0×10^{-5}[b]	3.7×10^{-3} (6.0×10^{-3})[d]	

[a] Average of two runs; maximum deviation ±50%. [b] Average of two runs; maximum deviation ±5%. [c] *This value will have the same* experimental uncertainty as k_1, (see footnote a). [d] This rate was computed from the data reported by Brown and Occolowitz.[2g] [e] Essentially the same ratio was obtained when exchange rates for (**3**) and (**4**) were measured individually under the above conditions.

---

† Hydrocarbon (**3**) was synthesized earlier by a more elaborate procedure.[2c] The compound obtained by the present method displayed spectroscopic characteristics identical to those reported in the literature.[2c]

‡ Compound (**4**) obtained by this method displayed spectroscopic characteristics identical to those reported in the literature.[2c]

second-order rate constants (k_2) were obtained by dividing k_1 by the base concentration. These results, together with k_2 for bicyclo-octadiene (**4**) computed from literature data,[2g] are shown in Table 1.

Examination of the data in Table 1 shows that k_2 for bicyclo-octadiene (**4**) obtained in the present study agrees well with that reported in the literature.[2g] More significantly, a comparison of the exchange rate of (**4**) with that of 3-phenylbicyclo-octadiene (**3**) shows that the phenyl group has brought about a rate enhancement of less than a factor of ten. This rate increase is well within the range expected from the inductive effect of a benzene ring, and leads to the conclusion that the bicyclo-octadienyl anion (**6**) must receive little, if any, homoaromatic stabilization. Since the presence of the phenyl group at C-3 is expected to facilitate and enhance long range π interactions, it must be concluded that the unsubstituted anion (**1**) would be an even less likely candidate for homoaromatic stabilization. Rather, as theoretical studies have suggested for quite some time, the unusual stability of (**1**) relative to its 6,7-dihydro analogue (**2**), must be attributed primarily to the inductive effect of the C-6,7 double bond,[3] although negative hyperconjugation and counterion interactions[3b] may also play a role.§

The authors thank Mark McDermot and Paul Zimerman for a number of preliminary experiments in relation to this project, and Dr. J. H. Carney for stimulating discussions. This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

Received, 4th October 1989; Com. 9/04239C

References

1 S. W. Staley, in 'Reactive Intermediates,' eds. M. Jones, Jr., and R. A. Moss, vol. 3, Wiley-Interscience, New York, 1985, pp. 27–30.

2 (a) R. R. Squires and R. E. Lee, *J. Am. Chem. Soc.*, 1986, **108**, 5078; (b) N. Hertkorn, F. H. Kohler, and G. Muller, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 468; (c) M. Christl and D. Bruckner, *Chem. Ber.*, 1986, **119**, 2025; (d) W. N. Washburn, *J. Org. Chem.*, 1983, **48**, 4287; (e) M. Christl, H. Leininger, and D. Bruckner, *J. Am. Chem. Soc.*, 1983, **105**, 4843; (f) W. Huber, K. Mullen, R. Buch, W. Grimme, and J. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 301; (g) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc. (B)*, 1968, 411.

3 (a) R. Lindh, B. J. Roos, and P. Ahlbert, *J. Am. Chem. Soc.*, 1986, **108**, 6554; (b) P. v. R. Schleyer, E. Kaufmann, A. J. Kos, H. Mayr, and J. Chandrasekhar, *J. Chem. Soc., Chem. Commun.*, 1986, 1583; (c) J. B. Grutzner and W. L. Jorgansen, *J. Am. Chem. Soc.*, 1981, **103**, 1372; (d) E. Kaufmann, H. Mayr, J. Chandrasekhar, and P. v. R. Schleyer, *ibid.*, 1981, **103**, 1375.

4 For a theoretical study supporting homoaromaticity in (**1**), see, J. M. Brown, R. J. Elliot, and W. G. Richards, *J. Chem. Soc., Perkin Trans. 2*, 1982, 485.

5 See, for example, Tolbert and Rajca's arguments in relation to their study of the potential homoaromatic nature of the cyclohexadienyl anion: L. M. Tolbert and A. Rajca, *J. Org. Chem.*, 1985, **50**, 4805. For an earlier study conducted in our laboratories on the effect of phenyl groups on charge delocalization in carbanions, see: G. B. Trimitsis and A. Tuncay, *J. Am. Chem. Soc.*, 1975, **97**, 7193.

6 The synthesis of 3-phenylbicyclo-octadiene (**3**) outlined in Scheme 1 parallels that reported recently by Negishi and co-workers for the synthesis of a series of biaryls: Ei-ichi Negishi, T. Takahashi, and A. O. King, *Org. Synth.*, 1987, **66**, 67.

7 (a) N. A. LeBel and R. N. Liesemer, *J. Am. Chem. Soc.*, 1965, **87**, 4301; (b) N. A. LeBel and R. J. Maxwell, *ibid.*, 1969, **91**, 2307.

---

§ For a recent study on the homoaromatic nature of anion (**1**) based on the NMR spectra of a number of phenyl substituted bicyclo-octadienes, including (**3**), see ref. 2c.