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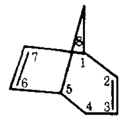
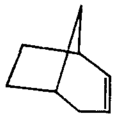
Effect of Stabilizing Groups on the Extent of Long Range π Electron Participation in Carbanions

Sir:

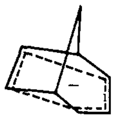
It has been recently reported by Brown and Occolowitz[1] that bicyclooctadiene (**1**) undergoes base-catalyzed hydrogen–deuterium exchange at C_4 $10^{4.5}$ times faster than its saturated analogue, monoene **2**. The increased reactivity of **1** was attributed to the greater stability of its incipient carbanion intermediate during deuterium exchange, in which the negative charge could interact not only with the carbon–carbon double bond at $C_{2,3}$ but also with the $C_{6,7}$ double bond, thereby producing a bishomoaromatic cyclopentadienyl species as represented by structure **3**. The participation of the $C_{6,7}$ double bond in delocalizing the negative charge was subsequently confirmed by Winstein and his co-workers[2] who were able to generate anion **3** in sufficiently large quantities to study its ^{1}H NMR spectrum. The latter clearly supported the delocalized nature of the anion.



1



2

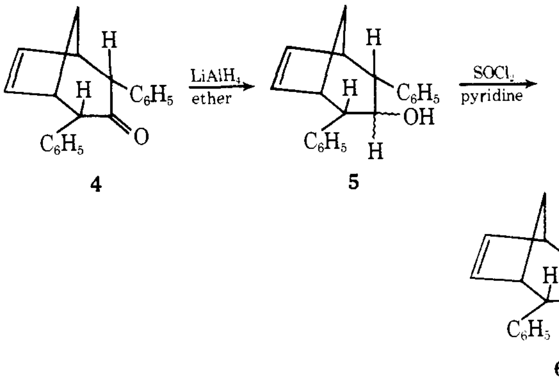


3

We now wish to report that replacement of the hydrogens at C_2 and C_4 in bicyclic diene **1** by phenyl groups results in totally eliminating the charge delocalization from C_4 to the carbon–carbon double bond at $C_{6,7}$. This conclusion was reached on the basis of the fact that 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (**6**) and its saturated analogue **9** were found to undergo base-catalyzed hydrogen–deuterium exchange at C_4 at essentially the same rate (Table I).

A number of reports have appeared in the recent literature indicating that the extent of neighboring group participation in stabilizing an incipient carbonium ion is inversely proportional to the stability rendered to the developing charge by groups directly attached to the cationic center.[3,4] In turn, this principle has been extensively used as a very effective tool in determining the extent of π and σ participation in a large variety of carbonium ions.[4,5] The present report constitutes the first study demonstrating that the above principle is equally applicable to carbanions stabilized by π electron participation.

Scheme I



2,4-Diphenylbicyclo[3.2.1]octa-2,6-diene (**6**) was synthesized as outlined in Scheme I. Thus, treatment of *cis-endo*-diphenyloctenone[6] (**4**) (40 mmol) in ether with 66 mmol of $LiAlH_4$ at reflux for 48 hr, followed by the usual work-up, afforded 8.0 g (73%) of alcohol[7] **5**: mp 78–83° from 95% ethanol; ir 3570 cm^{-1} (OH); ^{1}H NMR (DMSO-d_6) δ 2.12 (m, 2 H, H_8), 2.80 (m, 2 H, $H_{1,5}$), 3.05 (s, 1 H, OH), 3.32 (m, 2 H, $H_{2,4}$), 4.22 (m, 1 H, H_3), 6.49 (s, 2 H, $H_{6,7}$), 7.27 (m, 10 H, aromatic protons); mass spectrum[8] (relative intensities) 276 (M^+, 12%), 258 (19%), 157 (53%), 120 (30%), 91 (100%).

Alcohol **5** (29.7 mmol) was subsequently treated with purified thionyl chloride (44.6 mmol) in dry pyridine at room temperature for 6 hr to produce, after work-up and purification, 6.2 g (80%) of 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene[7] (**6**): mp 43–45° from methanol; ^{1}H NMR[9] ($CDCl_3$) δ 2.27 (m, 2 H, H_8), 3.05 (m, 1 H, H_5), 3.25 (m, 1 H, H_1), 3.82 (m, 1 H, H_4), 5.32 (doublet of doublets, 1 H, H_6), 5.72 (m, 1 H, H_3), 6.47 (doublet of doublets, 1 H, H_7), 7.31 (m, 10 H, aromatic); mass spectrum[8] (relative intensities) 258 (M^+, 71%), 230 (40%), 154 (40%), 105 (100%), 91 (82%).

2,4-Diphenylbicyclo[3.2.1]oct-2-ene (**9**) was synthesized as shown in Scheme II. Thus, bicyclooctenone (**4**) (38.3 mmol) was treated with *p*-toluenesulfonylhydrazine (56.4 mmol) and a catalytic amount of hydrochloric acid in methanol at reflux for 23 hr to afford, after work-up and purification, 8.3 g (78%) of diphenyloctanone[7,10] **7**: mp 114–116° from methanol; ir 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.02 (m, 6 H, H_8 and $H_{6,7}$), 2.78 (m, 2 H, $H_{1,5}$), 3.93 (d, 2

Scheme II

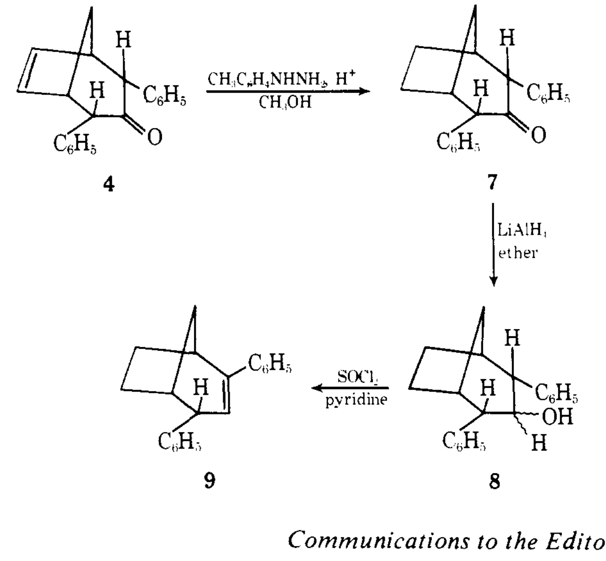


Table I. Second-Order Rate Constants of Hydrogen–Deuterium Exchange of Hydrocarbons

Hydrocarbon	k_2 (M^{-1} sec^{-1})
6[a,b]	0.50×10^{-2}
9[a,c]	0.15×10^{-2}
10[a,b,d]	0.33×10^{-2}
1[d,e]	2.0×10^{-3}
2[d,e]	0.7×10^{-7}

[a] Experiments were carried out at 25.0° in 87:13 DMSO-d_6–CH_3OD with CH_3ONa as the base. Rates are reproducible to less than ±10%. [b] Average of two runs. [c] Average of three runs. [d] The reported rate has been corrected for statistical factors. [e] The second-order rate constant for this compound has been computed on the basis of the data reported in ref 1a. Experiments were carried out at 60.0° in DMSO-d_6 with t-C_4H_9OK as the base.[1a]

H, $H_{2,4}$), 7.30 (m, 10 H, aromatic). Bicyclooctanone (**7**) was in turn reduced to the corresponding alcohol[7] **8**: mp 103–106°; ir 3420 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 1 H, OH), 2.04 (m, 6 H, H_8 and $H_{6,7}$), 2.73 (m, 2 H, $H_{1,5}$), 3.21 (m, 2 H, $H_{2,4}$), 4.69 (m, 1 H, H_3), 7.42 (m, 10 H, aromatic); mass spectrum[8] (relative intensities) 278 (M^+, 57%), 260 (3%), 171 (39%), 117 (41%), 91 (100%). Finally, alcohol **8** was dehydrated by means of thionyl chloride in pyridine to give 2,4-diphenylbicyclo[3.2.1]oct-2-ene[7] (**9**), in high yield; mp 53–55° from methanol; ^{1}H NMR ($CDCl_3$) δ 1.73 (m, 6 H, H_8 and $H_{6,7}$), 2.72 (m, 2 H, $H_{1,5}$), 4.03 (m, 1 H, H_4), 5.90 (m, 1 H, H_3), 7.33 (m, 10 H, aromatic); mass spectrum[8] (relative intensities) 260 (M^+, 27%), 219 (18%), 141 (39%), 130 (42%), 91 (100%).

The rates of base-catalyzed hydrogen–deuterium exchange of bicyclic hydrocarbons **6** and **9** as well as of *trans*-1,3-diphenylpropene[11] (**10**) were next examined. The latter compound was included as a reference system. The exchange experiments were carried out in 87:13 DMSO-d_6–CH_3OD containing CH_3ONa at 25°, and the deuterium uptake was monitored by mass spectroscopy.[12] The pseudo-first-order rate constants obtained experimentally were divided by the base concentration to afford the second-order rate constants shown in Table I.

Inspection of Table I shows that replacement of the hydrogens at C_2 and C_4 in bicyclic hydrocarbons **1** and **2** by phenyl groups has essentially eliminated the large rate difference of deuterium exchange between the two systems. Thus, while bicyclooctadiene (**1**) was found to exchange its allylic hydrogens $10^{4.5}$ times faster than monoene **2**, diphenylbicyclooctadiene (**6**) underwent deuterium exchange only 3.3 times faster than its saturated analogue **9**, strongly indicating that π electron participation in hydrocarbon **6** has been virtually totally eliminated. The slightly larger rate of bicyclic diene **6** relative to monoene **9** is most likely due to the stabilizing inductive effect of the $C_{6,7}$ double bond,[1a] rather than neighboring group effects. It should also be noted that the rates of both hydrocarbons **6** and **9** are in very close proximity to the exchange rate of *trans*-1,3-diphenylpropene, a system in which stabilization by means of neighboring group effects is not possible. On the basis of these results it can be concluded that just as in the case of carbonium ions, the extent of charge delocalization in carbanions has an inverse relationship to the stability rendered to the developing negative charge by groups directly attached to the carbanionic center.

With this principle, now firmly established for carbanions as well, its use as a tool in confirming the presence of long-range π electron participation in these intermediates should prove valuable.

Whether both phenyl groups are necessary for the elimination of electron participation in the carbanion derived from hydrocarbon **6** is not clear from the present study. The synthesis of a number of bicyclic systems whose exchange rates will help determine the minimum stabilization necessary to eliminate charge delocalization in this and other carbanions is currently under way.

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(6) Diphenyloctenone **4** was synthesized essentially as described by R. C. Cookson et al., *J. Chem. Soc. C*, 473 (1967), with some modifications.
(7) Satisfactory elemental analysis was obtained for this new compound.
(8) Mass spectra were recorded using a DuPont 21-490 mass spectrometer.
(9) Peak assignments were based on spin decoupling and INDOR experiments, using a Varian XL-100 NMR instrument.
(10) Diphenylbicyclooctanone **7** was also synthesized from **4** by hydrogenation over PtO_2 in ethanol.
(11) W. A. Bonner, *J. Org. Chem.*, **31**, 396 (1966).
(12) In a typical run, 3.86 mmol of bicyclic diene **6** was dissolved in 3.5 ml of DMSO-d_6 and 0.51 ml of CH_3OD in a 5-ml volumetric flask, and 0.03 ml of a 3.05 *M* stock solution of CH_3ONa in CH_3OD was added. The final base concentration after mixing was 1.83×10^{-2} *M*. The flask was immersed in a constant temperature bath at 25 ± 0.1°, and aliquots were withdrawn at varying time intervals over a period of 1.5 hr. The aliquots were quenched in a solution containing 10 ml of water and 1 ml of 3 *N* HCl and extracted with 30 ml of pentane. The organic solvent was dried and evaporated to give the partially deuterated diene **6**. The extent of deuterium incorporation was ascertained by low voltage mass spectroscopy.[8] The pseudo-first-order rate constant of the reaction was determined by plotting log H remaining vs. time. The second-order rate constants shown in Table I were obtained by dividing the pseudo-first-order rate constants by the base concentration.

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The Absolute Configuration of (+)D-Trisphenanthrolinecobalt(III)

Sir:

In recent years Mason and co-workers[1-4] have extensively applied exciton theory, based on the strongly CD active, long-axis polarized π–π^* ligand transitions, to the assignment of absolute configuration for trisphenanthroline complexes. A possible objection to this approach is the apparent neglect of the metal ion and covalency.[5] In order to accommodate this possibility, Hawkins and co-workers[5-7] have proposed an alternative procedure, involving an analysis of both CD and isotropic absorption data. In several instances, absolute configurations based on the two methods differ, the most notable case being that of $(+)_D$-$Co(phen)_3^{3+}$. Whereas the former method[8] yields a ΛC_3 assignment, Hawkins et al.[5] suggest the ΔC_3 absolute configuration. The validity of the isotropic absorption analysis has recently been questioned,[9] but the controversy still remains unresolved.