

## Homoaromaticity in Anions: The Effect of Electron Donor Groups

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Base-catalysed exchange of 2,4-di-*p*-anisoylbicyclo[3.2.1]octa-2,6-diene (**10**) proceeds faster than that of 2,4-di-*p*-anisoylbicyclo[3.2.1]oct-2-ene (**13**) indicating the significance of homoaromaticity in anions and the utility of the electron-demand tool to detect such interactions.

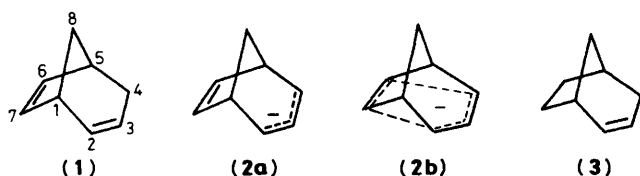
Homoaromaticity<sup>1</sup> in anions is currently under active investigation, both theoretically<sup>2</sup> and experimentally.<sup>3</sup> The bicyclo[3.2.1]octa-3,6-dien-2-yl anion (**2a**) is the most widely cited example of anionic homoaromaticity. Thus, facile exchange<sup>4</sup> in (**1**) as compared to (**3**) was attributed to the bishomoaro-

matic character of the intermediate carbanion (**2b**). Direct observation<sup>5</sup> of the <sup>1</sup>H n.m.r. spectrum of ion (**2**) provided additional support. However, some questions were raised concerning the interpretation of these n.m.r. experiments when we reported<sup>6</sup> that the 2,4-diphenyl derivative of (**1**)

**Table 1.** Second-order H-D exchange rate constants.<sup>a</sup>

Compound	$k/M^{-1}s^{-1}$
2,4-Di- <i>p</i> -anisoylbicyclo[3.2.1]octa-2,6-diene (10)	$0.25 \times 10^{-1}$
2,4-Di- <i>p</i> -anisoylbicyclo[3.2.1]oct-2-ene (13)	$0.31 \times 10^{-4}$
2,4-Diphenylbicyclo[3.2.1]octa-2,6-diene (14)	$0.50 \times 10^{-2}$
2,4-Diphenylbicyclo[3.2.1]oct-2-ene (15)	$0.15 \times 10^{-2}$

<sup>a</sup> Experiments were carried out in 87:13 (CD<sub>3</sub>)<sub>2</sub>SO-MeOD with MeONa as the base, in a constant temperature bath at 25 ± 0.1 °C, and aliquots were withdrawn at varying time intervals. After quenching, the solution was extracted with diethyl ether to obtain the partially deuterated samples. The extent of deuterium incorporation was ascertained by <sup>1</sup>H n.m.r. and low voltage mass spectroscopy. The pseudo first-order rate constant was determined by plotting log [H remaining] vs. time. The second-order rate constants shown in Table 1 were obtained by dividing the pseudo first-order rate constants by the base concentration. Rates are reproducible to ±10%.



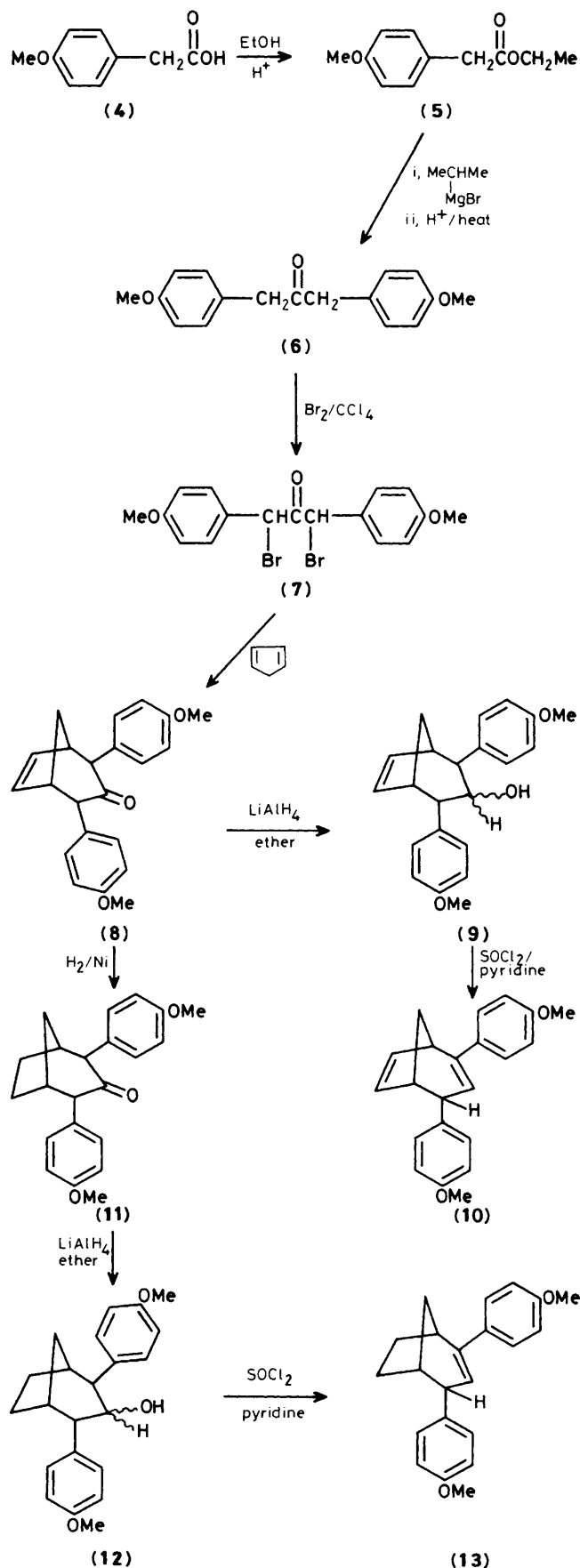
exhibited only a very weak kinetic acidity enhancement over the corresponding derivative of (3), yet showed upfield shifts which were comparable to those found for (2). Subsequently, several studies<sup>7</sup> appeared indicating that homoconjugation is insignificant for anions. Recent investigations<sup>3b-e</sup> provided evidence supporting a fully delocalized form (2b). Thus, more experimental data is needed to document the homoaromaticity in anions.

Our approach to the problem was to prepare 2,4-di-*p*-anisoylbicyclo[3.2.1]octa-2,6-diene (10) and 2,4-di-*p*-anisoylbicyclo[3.2.1]oct-2-ene (13) and use the electron-demand tool to detect homoconjugation. This tool has been used very effectively to determine the extent of  $\pi$  and  $\sigma$  participation in a large variety of cations.<sup>8</sup> If homoaromaticity is present in (1), the electron-donating *p*-methoxy groups should cause an increase in the acidity of (10) over (13) according to this principle.

Compounds (10) and (13) were synthesized<sup>†</sup> as shown in Scheme 1. Hydrogen-deuterium exchange experiments were carried out in (CD<sub>3</sub>)<sub>2</sub>SO-MeOD/MeONa and the deuterium uptake was monitored by <sup>1</sup>H n.m.r. and mass spectrometry. The relative rates of exchange for the allylic hydrogens (4-H) were 806:1 (Table 1).

Our data indicate that there is long-range  $\pi$  participation in the anion of (10) resulting in the enhanced kinetic acidity of (10) over (13). The increased reactivity of (10) is attributed to the greater stability of its incipient anionic intermediate during H-D exchange, in which the negative charge could interact not only with the C<sub>2,3</sub> double bond and the benzene rings but also with the remote C<sub>6,7</sub> double bond, thereby producing a homoaromatically stabilized bishomocyclopentadiene anion analogous to (2b). No such stabilization can be visualized in the case of the anion of (13). Our observations are compatible with the recent gas phase studies.<sup>9</sup> Inductive/field effects could be a likely alternative for homoconjugation as the cause of the increased acidity of (10). However, both the solution<sup>3e</sup> and the gas phase studies<sup>9</sup> have shown these to be minor in comparison to homoaromaticity.

<sup>†</sup> Satisfactory elemental and spectral analyses were obtained for compounds (8)-(13).

**Scheme 1**

Our studies also indicate that the stabilizing effect of a remote double bond seems to be a function of the electron demand of the incipient carbanion. The increased acidity of (10) over that of (14) and (15) (Table 1) reveals that as the anion gets less stable due to the electron-releasing effects of methoxy groups, bishomoaromaticity becomes more evident in stabilizing it. Our investigations thus demonstrate for the first time that, as in the case of cations, the electron demand tool may be used effectively to detect homoaromaticity in anions.

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