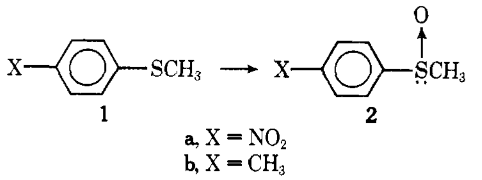
electrode in a benzene solution of the anhydride for 24 h. The resulting material was used under the usual conditions to convert **1a** to **2a**. The product was again optically inactive.



Other experiments showed that the modified DSA electrode gave identical optical yields in three consecutive runs and that there was little dependence of optical yield on the potential used. There are, however, differences in the voltammograms of **1a** on modified and unmodified surfaces. These will be reported on and analyzed in a full publication.

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Carbanion Chemistry. A Room Temperature Retro-Diels-Alder Reaction

Sir:

The retro-Diels-Alder reaction commonly requires temperatures of 150 °C or more for convenient reaction.[1,2] The extensive chemistry of norbornene and norbornadiene provides ample demonstration of the resistance to thermolysis.[3] In striking contrast we now report that the 7-phenylnorbornenyl anion I undergoes the retro-Diels-Alder reaction within 30 min

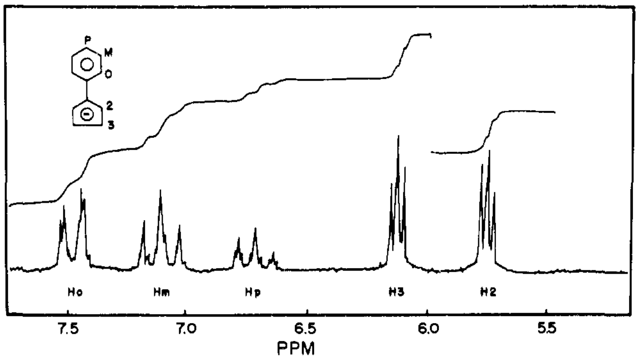
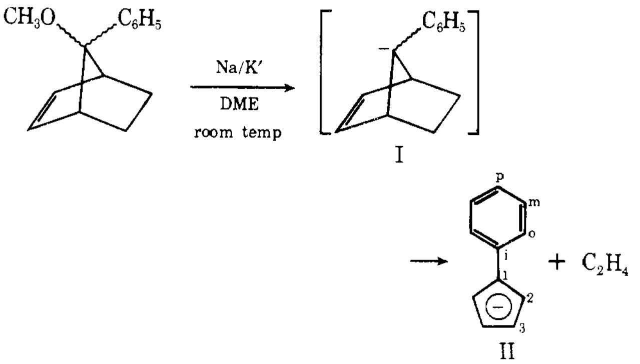


Figure 1. The 100-MHz ^1H NMR spectrum of phenylcyclopentadienide ion in DME-d_{10}. Chemical shifts are shown in δ units from internal Me_4Si.

at room temperature. When a 1:3 mixture of *syn*- and *anti*-7-phenyl-7-methoxynorbornene[4] was stirred at room temperature with excess sodium-potassium alloy in 1,2-dimethoxyethane in an evacuated reactor,[5] gas evolution was observed and a deep green[6a] solution formed over a period of 30 min. The gas was collected and mass spectrometric analysis identified it as ethylene contaminated with solvent, 1,2-dimethoxyethane. The yield of ethylene was estimated to be 60% from mass spectrometric analysis. An NMR sample of the filtered solution in DME-d_{10} showed a clean spectrum of the phenylcyclopentadienide ion, II (Figure 1), as the only other species present. A ^{13}C NMR spectrum[6b] confirmed this conclusion. It is noteworthy that neither of the starting materials nor any other products were detected within the 5% limits set by sensitivity criteria. The structure of ion II was deduced from the characteristic phenyl anion absorptions and the AA′BB′ pattern of a monosubstituted cyclopentadiene in the proton spectrum. Proton decoupling confirmed the coupling interactions. When the anion solution was poured into ethanol, the color immediately discharged, but the transparent mixture darkened and turned black within 5 min. No low molecular weight product was obtained from a subsequent ether extract. This observation is consistent with the known chemistry of phenylcyclopentadienes.[7]



In an analogous pair of reactions, *syn*- and *anti*-9-phenyl,9-methoxybenzonorbornene were separately cleaved at −40 °C by Cs/K/Na alloy.[8] In 2 h at 0 °C gas evolution was complete yielding a clean solution of the 2-phenylindenide anion as the sole product. The proton spectrum showed a singlet 6.20 (H1), an AA′BB′ pattern 6.30, 7.00 (H4, H5, respectively), and the characteristic phenyl anion pattern at 6.78 (Hp), 7.15 (Hm overlapping H5), and 7.62 (Ho). Methanol quench yielded 2-phenylindene.

These observations now provide a rational explanation for several literature reports. Treatment of norbornadiene with amyl sodium gave a quantitative yield of the cyclopentadienyl anion and acetylene in 5 h.[11] When 7-*tert*-butoxynorbornadiene was cleaved with sodium/potassium alloy, only a 20%

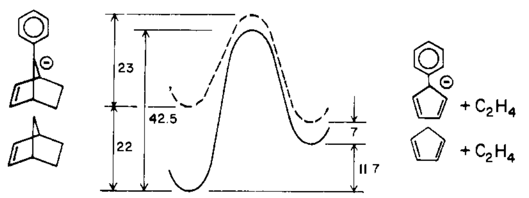


Figure 2. Free energy diagram for norbornene (ref 3a) and approximate free energy diagram for the 7-phenylnorbornenyl anion. Energies are shown in kilocalories per mole.

yield of norbornadiene was obtained.[12] Related Grignard and alkyl lithium reagents have proved to be elusive for synthetic purposes.[13] Base catalyzed exchange studies of norbornenyl systems[14] indicate that the 7-norbornenyl anion is an intermediate with finite lifetime. However, the claim[15] that the 7-norbornenyl anion was generated by oxidative nitrogen loss must be treated with caution, because of the implicit requirement that anion inversion be faster than carbanion quench by solvent water.

A crude analysis of reaction energetics is instructive. Walsh and Wells[3] have established that ethylene loss from norbornene requires 42.5 kcal/mol activation energy (extrapolated to 25 °C). A lower limit of 38 kcal/mol may be inferred for acetylene loss from 7-phenylnorbornadiene.[3d] In striking contrast, the ethylene loss from 7-phenylnorbornenide ion has an activation energy ≤ 23 kcal/mol. A comparison of energetics is shown in Figure 2. The relative energies of the carbanions were estimated from pK_a data and are accurate to ± 3 kcal/mol at best.[16] The significant conclusion to be drawn is that *anions are efficient bond-breaking species* provided the thermodynamics are favorable. Reference 17 lists several recent examples of this principle. A wide variety of classical anionic condensation reactions (e.g., Robinson annulation) are based on this principle as they rely on facile reversibility for their success.[18]

The importance of the counterion in controlling anion reactions has been noted repeatedly.[17b,d,e,i] The preparation and subsequent reaction of 7-norbornenyl Grignard reagents[13] is indicative that counterion control is also significant in the present case. Finally it is interesting to compare the carbanion with its heterocyclic analogues. Diels-Alder reactions are rare in pyrrole chemistry, not because addition is difficult, but because the reverse reaction occurs readily.[19] By contrast furan and especially isobenzofuran are efficient dienes in the Diels-Alder reaction.[20] The combination of lower aromatic stabilization in the diene and the high degree of lone pair localization on oxygen in the adduct are presumably responsible.[21]

We are currently investigating the synthetic and mechanistic potential of the cleavage. Incorporation of an appropriate norbornadiene as a dienophile in a Diels-Alder reaction followed by anion generation and the retroreaction should provide a convenient acetylene equivalent for Diels-Alder processes.

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Molecular Beam Chemistry: Reactions of Cs^+ with Chlorobenzene and the Electronic State of the Phenyl Cation

Sir:

Crossed molecular beam scattering experiments with Cs^+ on α-, *o*-, *m*- and *p*-chlorotoluene have recently been reported.[1,2] The results suggest that the product $C_7H_7^+$ is benzyl in the first case and tropylium for the others.[3] Moreover, the stripping process responsible for the forward scattering of the $C_7H_7^+$ leaves these ions with little internal excitation, while the repulsive or knock-out process responsible for the backward scattering produces excited benzyl ion in the α case and excited tropylium in the meta and para cases. The data suggest, in fact, that these ions are in their first excited singlet states. Further evidence for the strong electronic correlation in these systems is that over the range of collision energies from 0 to 15 eV, the only products that are observed ($C_7H_7^+$, $C_5H_5^+$, and $C_4H_3^+$) are those which have singlet (ground) states. We report here results of similar experiments with chlorobenzene,

$$Cs^+ + C_6H_5Cl \rightarrow CsCl + C_6H_5^+ \quad (1)$$

$$\rightarrow CsCl + C_2H_2 + C_4H_3^+ \quad (2)$$

These reactions, like the chlorotoluene reactions, are endoergic (by 4.4 eV for (1) and 7.7 eV for (2)[4]). The phenyl ion should resemble the tolyl ion, except that rearrangement to a "stable" singlet structure like tropylium is not possible.[5]

The experimental procedure is described in detail elsewhere.[1,6] Briefly, the Cs^+ ion beam and the thermal (300 K) C_6H_5Cl beam sources are mounted from a rotatable platform