Communications to the Editor

Deprotonation of Acenaphthene. The Acenaphthylene Dianion

Sir:

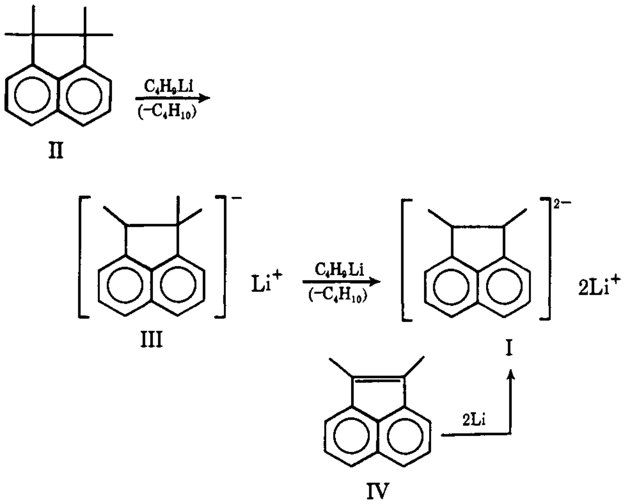
Consecutive one- and two-electron reduction of olefinic and aromatic compounds (R) by alkali metals (M) is a well-established method for the production of radical anions ($R\cdot^-$) and dianions[1] (R^{2-}, eq 1a). In principle, an alternative pathway to the same dianion is *via* deprotonation of the monoanion (RH^-) obtained by proton abstraction from a 1,2-dihydroolefin or aromatic (RH_2) by means of a metal alkyl (R'M, eq 1b). In fact, no prior example is recorded for the preparation of a dianion, formally bearing unit negative charge on adjacent carbons, by process 1b.[2] Inasmuch as common conditions of solvent and cation can be utilized for eq 1a and 1b, the relatively difficult proton loss from RH^-, as compared to electron transfer to $R\cdot^-$, must be attributed to kinetic factors reflecting the greater charge repulsion in the transition state for the formation of R^{2-} *via* eq 1b.

$$\begin{tikzcd} R \arrow[r, "M"] & R\cdot^{-} \arrow[dr, "M"] & & \text{(1a)} \\ & & R^{2-} & \\ RH_2 \arrow[r, "R'M", "(-R'H)"'] & RH^{-} \arrow[ur, "R'M", "(-R'H)"'] & & \text{(1b)} \end{tikzcd}$$

This electrostatic constraint is no longer operative for abstraction of a nonadjacent proton and examples of dianion formation by 1,4 and 1,5 deprotonation are available. Thus, 9,10-dihydroanthracene forms mono- and then dianion by consecutive proton abstraction with BuLi in THF,[5] but similar treatment of 9,10-dihydrophenanthrene gives no evidence[6] for dianion formation.[7] An even more graphic demonstration of this vicinal charge destabilization is apparent from the observation that abstraction of only one of the ring protons from 1,2,3,4-tetraphenylcyclobutene is possible,[8] despite the potential aromaticity of this dianion, whereas, under similar conditions, 1,5 dideprotonation is readily achieved from a molecule which forms a perturbed (antiaromatic) [12]annulene dianion.[9]

This sizable kinetic barrier to the formation of R^{2-} by neighboring proton abstraction from RH^- contrasts sharply with our present finding that acenaphthene (II) readily forms a dianion by precisely such a process. Even more remarkable is the finding that the rate of formation of R^{2-} is *faster* than that of RH^-.

Treatment of acenaphthene (II) with 1 equiv of *n*-butyllithium in THF at 0° for 1 hr gives a deep green solution of an anionic species which, after quenching with D_2O, affords 50% unchanged II and 50% of a new, isomeric hydrocarbon incorporating an average of two deuteriums per molecule.[10] Increasing the ratio of base to 2 equiv/mol of II gives a 95% yield of the dideuterated hydrocarbon. Exactly analogous results were obtained with methyl iodide as the quenching agent (see below). The identity of I to the dinegative ion of acenaphthylene (IV) was confirmed by prolonged reduction of IV with lithium metal in THF to yield a deep green solution whose nmr spectrum was closely similar to that reported[11] for the disodium anion of IV, and the quenching of which yielded products identical with those obtained from I prepared from II.[12]



These data, coupled with our inability to detect III as a stable species, are best accommodated by two alternatives (eq 2 and 3), both unprecedented. Either

$$\text{II} \xrightarrow[k_1]{-H^+} \text{III} \xrightarrow[k_2]{-H^+} \text{I} \qquad (2)$$

$$\text{II} \xrightarrow{-2H^+} \text{I} \qquad (3)$$

$k_2 \gg k_1$ so that a significant concentration of monoanion III never accumulates (eq 2),[13] or dianion I is produced directly by a two-proton abstraction by butyllithium aggregates (eq 3). Routes 2 and 3 can be distinguished by a deuterium isotope effect. Consecu-

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[1] E. deBoer, *Advan. Organometal. Chem.*, **2**, 115 (1964).

[2] We exclude from consideration here those dianions in which charge is delocalized to hereroatoms[3] as well as those obtained by proton abstraction from sp-hybridized carbon.[4]

[3] T. M. Harris and C. M. Harris, *Org. React.*, **17**, 155 (1969).

[4] R. West and G. A. Gornowicz, *J. Amer. Chem. Soc.*, **93**, 1720 (1971), and references cited therein.

[5] R. G. Harvey and C. C. Davis, *J. Org. Chem.*, **34**, 3607 (1969).

[6] Unpublished results, this laboratory.

[7] The preparation of the dianions of both anthracene and phenanthrene by method 1a has been reported by N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, **89**, 207 (1967).

[8] H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *ibid.*, **87**, 3019 (1965).

[9] B. M. Trost and P. L. Kinson, *ibid.*, **92**, 2591 (1970).

[10] Though the total amount of deuterium incorporation is always 2.0 ± 2%, the distribution of deuterium is strongly dependent on the method of quenching. This extraneous complication can be minimized by inverse addition with very rapid quenching. The details of this proton scrambling phenomenon will be reported in a future publication.

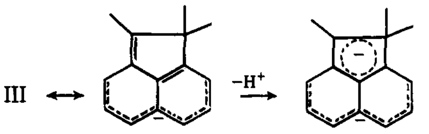
[11] R. G. Lawler and C. V. Ristagno, *J. Amer. Chem. Soc.*, **91**, 1534 (1969).

[12] Direct nmr characterization of I prepared from II was precluded by the presence of a small amount (<5%) of a paramagnetic artifact, identified by its esr spectrum as the acenaphthylene (IV) radical anion. We are grateful to B. Loy, Physical Research Laboratory, The Dow Chemical Co., Midland, Mich., for the esr investigation.

[13] An alternative to eq 2 involves disproportionation of 2 mol of RH^- to 1 mol each of RH_2 and R^{2-}. Though such a process has been established for tetracene and pentacene when R^{2-} is protonated,[7] we regard it as highly unlikely in the presence of excess butyllithium. However, HMO calculations indicate that such a disproportionation is thermodynamically favored by approproximately 0.8β.

tive proton abstraction (eq 2, $k_2 \gg k_1$) would be expected to have[14] $k_H/k_D \cong 7$, while a simultaneous two-proton loss would require $k_H/k_D \cong (7)^2$. The conversion of II (12 mg in 5 ml of THF) to I at 0° using a tenfold excess of butyllithium (25% in hexane) was monitored by the increase of the 5800-Å band of I. Under these conditions the reaction was first order in II over 90% of its lifetime and had $k_H = 8.8 \times 10^{-4}$ sec^{-1}. A similar investigation using 1,1,2,2-tetradeuterioacenaphthene[15] gave $k_D = 10.1 \times 10^{-5}$ sec^{-1}. Accordingly, the deuterium isotope effect, k_H/k_D = 8.7, rules out eq 3 and supports monometalation of II (k_1 in eq 2) as rate determining.

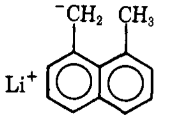
To account for the greatly enhanced acidity of the protons in the monoanion I over those in the neutral hydrocarbon II, we stress the presence of the cyclopentadienoid character generated in monoanion III by charge delocalization, as illustrated in IIIa. Loss of the exceptionally acidic proton from IIIa produces



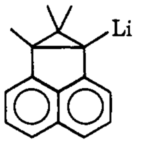
IIIa Ia

dianion Ia, an auspicious combination of cyclopentadienyl and heptatrienyl anions, both well-established species.[16]

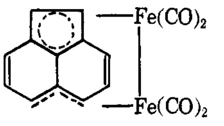
In support of IIIa we note that related compounds in which the cyclopentadiene ring is absent (as in 1,8-dimethylnaphthalene[6]) or is sterically inhibited (as in cycloprop[*a*]acenaphthene[17]) form only stable monoanions (V and VI, respectively) even when treated with a large excess of butyllithium for prolonged periods. Precedence for Ia is found in a binuclear, organometallic complex obtained from IV and $Fe_3(CO)_{12}$ which has been shown to have structure VII by an X-ray diffraction



V



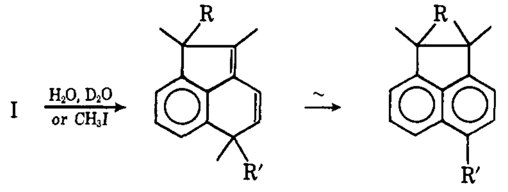
VI



VII

study.[18] The isolated cyclopentadienyl and allyl π systems of VII are readily extrapolated to the cyclopentadienyl–heptatrienyl π systems of Ia when the covalent iron atoms are replaced by ionic lithiums.

Protonation of I proceeds as predicted[19] and affords 1,5-dihydroacenaphthylene (VIII) in 95% yield. Similarly the 1,5-dideuterio (IX) and 1,5-dimethyl (X) analogs are obtained by quenching with D_2O and methyl iodide, respectively. Structural assignment for VIII–X is based on their nmr and uv spectra which closely parallel those for the known[20] trityl-substituted compound XI. The facile 1,5-H rearrangement of VIII, IX, and X to their thermodynamically favored acenaphthene isomers (II, XII, and XIII) is subject to a



VIII, R = R′ = H
IX, R = R′ = D
X, R = R′ = CH_3
(XI, R = $(C_6H_5)_3C$; R′ = H)

XII, R = D; R′ = H or D
XIII, R = R′ = CH_3

variety of catalytic effects and will be described in detail in a subsequent publication.

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(14) *Cf.*, Y. Pocker and J. H. Exner, *J. Amer. Chem. Soc.*, **90**, 6764 (1968); P. West, R. Waack, and J. I. Purmont, *J. Organometal. Chem.*, **19**, 267 (1969).

(15) Prepared by two exchanges of II in DMSO-d_6 (99.5%) containing potassium *tert*-butoxide. II-*1,1,2,2-d*$_4$ retained less than 1% of benzylic protons as shown by nmr and mass spectra.

(16) H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88**, 1084 (1969), and R. B. Bates, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4608 (1969), have prepared and characterized the heptatrienyl anion.

(17) G. Wittig, V. Rautenstrauch, and F. Wingler, *Tetrahedron, Suppl.*, No. 7, 189 (1966).

(18) M. R. Churchill and J. Wormald, *Chem. Commun.*, 1597 (1968).

(19) A. Streitwieser and S. Suzuki, *Tetrahedron.*, **16**, 153 (1961).

(20) G. Wittig, H. G. Reppe, and T. Eicher, *Justus Liebigs Ann. Chem.*, **643**, 47 (1961); W. Tochtermann and B. Knickel, *Chem. Ber.*, **102**, 3508 (1969).

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Correlation between Multiple Charge-Transfer Bands and Radical Absorption as Exemplified with Pyridinium Compounds

Sir:

Multiple charge-transfer bands in donor–acceptor complexes have been assigned to transitions *from* two upper occupied levels in the donor[1] or *to* two lower unoccupied levels in the acceptor.[2,3] Isomeric complexes have also been postulated[4] but are difficult to justify.[3] In the case of the 1-alkylpyridinium iodides, the two charge-transfer bands observed in nonpolar solvents were once assigned to the formation of $^2P_{3/2}$ and $^2P_{1/2}$ iodine atoms in the excited state, on the basis that the separation between the two bands (ΔTE) corresponded exactly to that expected for the formation of iodine atom in two states in the case of 1-methylpyridinium iodide.[5] However, the marked variation in the magnitude of ΔTE with the position of substitution on the pyridinium ring was not easily explained in this way [$\Delta TE(4-) > \Delta TE(2-) = \Delta TE$(unsubsd) $> \Delta TE(3-)$].[5] Some parallelism between the variation in ΔTE values for dimethylaniline and iodide ion as donors to pyridinium ions led to the suggestion that two acceptor levels of the pyridinium ion were involved.[6] This idea has received strong support from the poor correlation of the ΔTE values with polarographic reduction potentials of pyridinium ions[7] in the face of

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(1) E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, **86**, 3930 (1964).

(2) S. Iwata, J. Tanaka, and S. Nagakura, *ibid.*, **88**, 894 (1966).

(3) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, pp 67-72.

(4) H. Cauquis, O. Chalvet, and Y. Thibaud, *Bull. Soc. Chim. Fr.*, 1015 (1971).

(5) E. M. Kosower, J. A. Skorcz, W. M. Schwarz, Jr., and J. W. Patton, *J. Amer. Chem. Soc.*, **82**, 2188 (1960).

(6) J. W. Verhoven, I. P. Dirkx, and Th. J. de Boer, *Tetrahedron*, **25**, 3395 (1969).

(7) R. A. Mackay, J. R. Landolph, and E. J. Poziomek, *J. Amer. Chem. Soc.*, **93**, 5026 (1971).