(new, bp 106–107° (2 Torr)) are easily available by the Hennion route.[14] Finally, it should be emphasized that LiTMP, LiN(t-Am)t-Bu, and LiETA *cannot* transfer an α hydride to substrates containing actual or latent Lewis acid sites ($A + H{-}C{-}B \rightarrow A{-}H + C{=}B^+$), a major side reaction in syntheses with other $LiNR_2$ bases.[15,16] Other assays follow.

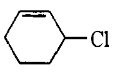
The reaction of ArCl with bases is potentially a most economical source of benzynes.[16] However, this method, though often used in synthesis (especially with the more reactive[17] but also more costly ArBr), is severely limited in scope because the base itself generally adds more efficiently to the benzyne than other substrates included in the reaction medium. Of those reagents capable of removing HX from ArX, LiR is particularly notorious in this respect while $NaNH_2$–NH_3 and KNH_2–NH_3 are ranked with the bases least likely to react with the derived benzynes.[16] As another assay of the value of LiTMP, the yields of m-methoxytolane (IV) obtained from treatment of o-chloroanisole with $LiNR_2$ and LiC≡CPh are listed in Table I. Published attempts to accomplish this transformation with o-bromoanisole and $NaNH_2$ gave only tars[17] (even the yield of tolane from PhBr by this latter method was only 26% [or less; mp 51–60°[17]]). In a second comparison pure Ph_2S was isolated (93%) from PhCl, PhSLi, and LiTMP *vs.* a reported 41% (estimated, no isolation) from PhBr, PhSK, and KNH_2.[17] Preliminary experiments indicate that yields in other known arylations of carbanions[16] also are increased substantially using the ArCl–LiTMP procedure. However, efforts to make the known benzyne–furan adduct[16] by this route failed.

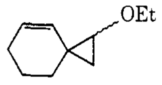
In carbonyl condensation chemistry the syntheses, A with R = Me or Et, are considered among the most stringent empirical measures of the strength and selective reactivity desired in candidate bases (B^-) and of the inertness required in BH.[18] In these assays the failure

$$\underset{\text{A}}{R_2CHCO_2Et} \underset{BH}{\overset{B^-}{\rightleftharpoons}} [R_2\bar{C}CO_2Et] \xrightarrow{PhCOCl} \underset{\substack{\text{V, R = Me}\\ \text{VI, R = Et}}}{PhCOCR_2CO_2Et}$$

of RMgX, LiR, NaOEt, NaH, and $NaNH_2$ has been used to demonstrate the utility of triphenyl methide bases ($NaCPh_3$: V, 50–55%; VI, 41%; $KCPh_3$: V, 50%; VI, 22%; $KCPh_2(p\text{-}Me_2NCH_2Ph)$: V, 40%; VI, 22%).[18] The inferiority of NaN(i-Pr)$_2$ (V, 14%[18]) and $LiN(SiMe_3)_2$ (V, <10%, this work) has also been shown. Examination of the final column in Table I exposes the yield advantage of using LiTMP as the base in ester condensations—a superiority further enhanced by the simplicity of removal of HTMP (*vs.* Ph_3CH) from neutral reaction products.

The use of LiTMP and its congeners to accomplish previously unrealized transformations is now under active investigation. In this context it is pertinent that VII undergoes α (and not β or 1,4) elimination with


VII



VIII

LiTMP in $EtOCH{=}CH_2$ (→ VIII, ~1:1 syn:anti, new, bp 84–85° (14 Torr)).[19]

Acknowledgments. We thank Dr. Jack Baldwin for valuable advice. We are also grateful to the National Science Foundation (GP-10834) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (3992-A), for financial support.

---

[13] However, the literature route [overall 0.7% *via* t-BuMgCl: F. Klages and H. Sitz, *Chem. Ber.*, **92**, 2606 (1959)] has been superceded by a better combination of known methods: $KMnO_4$ oxidation of t-$BuNH_2$ to t-$BuNO_2$, then Na reduction and HCl hydrolysis to t-$Bu_2NOH \cdot HCl$, and finally reduction with iron in aqueous HCl (overall 17%).

[14] In which the product is obtained by hydrogenation of RNHCR′R″C≡CH (from treatment of a ketone acetylene adduct first with HCl and then RNH_2): N. R. Easton, R. D. Dillard, W. J. Doran, M. Livezey, and K. E. Morrison, *J. Org. Chem.*, **26**, 3772 (1961), and references therein; *e.g.*, in the preparation of HETA, the commercial precursors are cyclohexanone and diisobutylenamine.

[15] For examples of ArX reduction (*via* benzyne) with $LiNR_2$ see Table 2.1 in ref 16.

[16] R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

[17] F. Scardiglia and J. D. Roberts, *Tetrahedron*, 3, 197 (1958), and ref 16.

[18] D. F. Thompson, P. L. Bayless, and C. R. Hauser, *J. Org. Chem.*, **19**, 1490 (1954); B. E. Hudson and C. R. Hauser, *J. Amer. Chem. Soc.*, **63**, 3156, 3163 (1941); C. R. Hauser and W. B. Renfrew, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 268.

[19] For a review of the intramolecular cyclization of simple vinylcarbenes (carbenoids) and trapping studies involving more complex systems see: W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

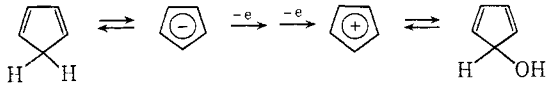
R. A. Olofson,* C. M. Dougherty
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

Received July 26, 1972

Electrochemical Determination of pK_{R^+} for Some Antiaromatic Cyclopentadienyl Cations

Sir:

Previous kinetic work[1] in our laboratory has established that cyclopentadienyl cation ($C_5H_5^+$) is a destabilized antiaromatic species although we now have some evidence[2] that the cation can be prepared under extreme conditions. Standard chemical methods for determining its pK_{R^+} are thus out of the question. However, we have shown that electrochemical techniques are useful for generating other unstable 4π-electron antiaromatic systems such as cyclopropenyl anions[3] and cyclobutadienes,[4] and determining their energies. In particular, we could determine the pK_a values of some cyclopropenyl anions[3] by using the pK_{R^+} values of the corresponding cations and the potentials required to reduce them to the anions. We now wish to report that the same thermodynamic cycle can be used, in reverse, to derive the pK_{R^+} values of cyclopentadienyl cations from the pK_a values of the corresponding anions.



---

[1] R. Breslow and J. M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972).

[2] R. Breslow, J. M. Hoffman, Jr. C. Perchonock, M. Saunders, R. Berger, A. Jaffe, and J. M. McBride, unpublished work.

[3] (a) R. Breslow and K. Balasubramanian, *ibid.*, **91**, 5182 (1969); (b) R. Breslow and W. Chu, *ibid.*, **92**, 2165 (1970); (c) R. Breslow and W. Chu, *ibid.*, in press.

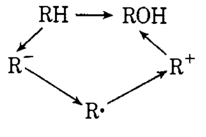
[4] R. Breslow, R. Grubbs, and S.-I. Murahashi, *ibid*,, **92**, 4139 (1970).

Table I. Oxidation Potentials[a]

System	pK_a	E_1	E_2	pK_{R^+} derived	pK_{R^+} other methods
Triphenylmethyl	31.5[b]	−1.335[e]	+0.312[f] +0.36[d,f]		−6.63[c]
9-Phenylfluorenyl	18.5[g]	−0.77[f]	+0.76[f]	−10.8	−10.5[h]
1,2,3-Triphenylindenyl	17.8 ± 3[i]	−0.567[e]	+0.76[f]	−12.6	−12.6[h]
Pentaphenylcyclopentadienyl	16.9 ± 3[j]	−0.354[e]	+0.94[f]	−18.9	<−16[h]
Cyclopentadienyl	18.5[k]	−0.03[f]	+1.77[f]	−40	

[a] In 0.2 *M* $LiClO_4$–DME at a platinum electrode measured *vs.* Ag|AgCl(s). [b] A. Streitwieser, E. Ciuffarin, and J. H. Hammers, *J. Amer. Chem. Soc.*, **89,** 63 (1967). [c] N. Deno, J. Jaruzelski, and A. Schriesheim, *ibid.*, **77,** 3044 (1955). [d] From reduction of triphenylmethyl perchlorate. [e] Near reversible behavior. [f] Irreversible behavior. [g] C. H. Langford and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **82,** 1503 (1960). [h] Reference 7. [i] By equilibration with 9-phenylfluorenyl, ref 6. [j] By equilibration with 1,2,3-triphenylindenyl, ref 6. [k] R. Breslow and W. Washburn, *J. Amer. Chem. Soc.*, **92,** 427 (1970).

Our method makes use of the following imaginary chemical cycle



The thermodynamic expression representing this cycle is

$$\Delta\Delta G_f^\circ = 2.3RTpK_a + FE_1 + FE_2 + 2.3RTpK_{R^+} - \sum\Delta G_S$$

where $\Delta\Delta G_f^\circ$ represents the difference in free energy of formation of the alcohol and of the hydrocarbon, E_1 and E_2 represent the first and second half-wave potentials for oxidation of the carbanion, and pK_a and pK_{R^+} have their usual significance. The last term of the equation represents the sum of all changes in free energy of solvation throughout the cycle, since no single solvent is appropriate for the determination of pK_a, pK_{R^+}, and the electrochemical measurements.

In practice, the term $[\Delta\Delta G_f^\circ + \Sigma\Delta G_S]$ was evaluated for the case R = triphenylmethyl, and assumed to be the same for the other tertiary systems. The electrochemical data were obtained by cyclic voltammetry of a solution of triphenylmethyllithium in 0.2 *M* $LiClO_4$–1,2-dimethoxyethane[5] and were used in conjunction with the best available values of pK_a and pK_{R^+}. These data are shown in Table I along with the data for four systems which feature a cyclopentadienyl nucleus. Values for pK_{R^+} were then derived for each of these systems utilizing values of pK_a available in the literature or determined by base-catalyzed equilibration with a hydrocarbon of known pK_a.[6] The electrochemical data for all systems were obtained under identical conditions.

The excellent agreement between derived values of pK_{R^+} and values previously reported from direct equilibration studies[7] for 9-phenylfluorenyl and 1,2,3-triphenylindenyl provides gratifying support for our method and assumptions. In the case of pentaphenylcyclopentadienyl, a previous attempt to measure pK_{R^+} by direct equilibration had been frustrated by rearrangement of the cation.[7] The value derived here, −18.9, is consistent with the earlier estimate that the true value would prove to be less than −16.

Unfortunately, the most interesting result reported in Table I also has the largest uncertainty. The determination of pK_{R^+} for $C_5H_5^+$ itself was complicated by three factors. Firstly, the electrochemical oxidation of cyclopentadienyllithium was accompanied by rapid formation of secondary products which deposited on and altered the properties of the electrode surface. The result is that the reported half-wave potentials for this system may be in error by as much as 0.1–0.2 V (about 4 p*K* units). Secondly, $\Delta\Delta G_f$ may well be constant for the series of tertiary systems but will very likely be somewhat different for the secondary parent system. A small correction for this was made using heats of formation calculated from Benson's thermodynamic parameters.[8] Lastly, the assumption that $\Sigma\Delta G_s$ is constant may also be in error for this case, since one might anticipate a difference in solvation energies comparing highly delocalized tertiary ions with smaller secondary ions. (A similar error is implicit in methods employing H_R for the direct determination of pK_{R^+}.)

These studies show that the electrochemical connection of thermodynamic data on carbanions (pK_a values) with data on carbonium ions (pK_{R^+} values) is reciprocal and reliable. Both can of course also be connected to radicals, and indeed bond dissociation energies for a variety of interesting species are easily derived from our data. The pK_{R^+} of −40 we find for cyclopentadienyl cation is remarkably low compared with values for other conjugated systems (*e.g.*, allyl cation[9] $pK_{R^+} \sim -20$). Thus these data are fully consistent with the proposition that $C_5H_5^+$ is a destabilized antiaromatic compound.

---

(5) The near reversibility of the first oxidation wave for triphenylmethyllithium may be taken as evidence that the species is largely dissociated in this medium. Since the other hydrocarbons represented in this study are considerably more acidic than triphenylmethane, it is unlikely that covalent carbon–lithium bonds represent a significant source of error.

(6) Mixtures of the two hydrocarbons and their lithio derivatives in 1,2-dimethoxyethane (0.1 *M* in *tert*-butyl alcohol) were allowed to equilibrate. The mixtures were quenched by inverse addition to acetic acid-*O-d* and the recovered hydrocarbons analyzed by mass spectrometry.

(7) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83,** 3727 (1961).

(8) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(9) R. Breslow, *Pure Appl. Chem.*, **28,** 111 (1971).

R. Breslow,* S. Mazur
Department of Chemistry, Columbia University
New York, New York 10027

Received October 2, 1972