PYRACYLENE DIANIONS

Barry M. Trost,[1] David Buhner, and G. Michael Bright

Department of Chemistry, University of Wisconsin
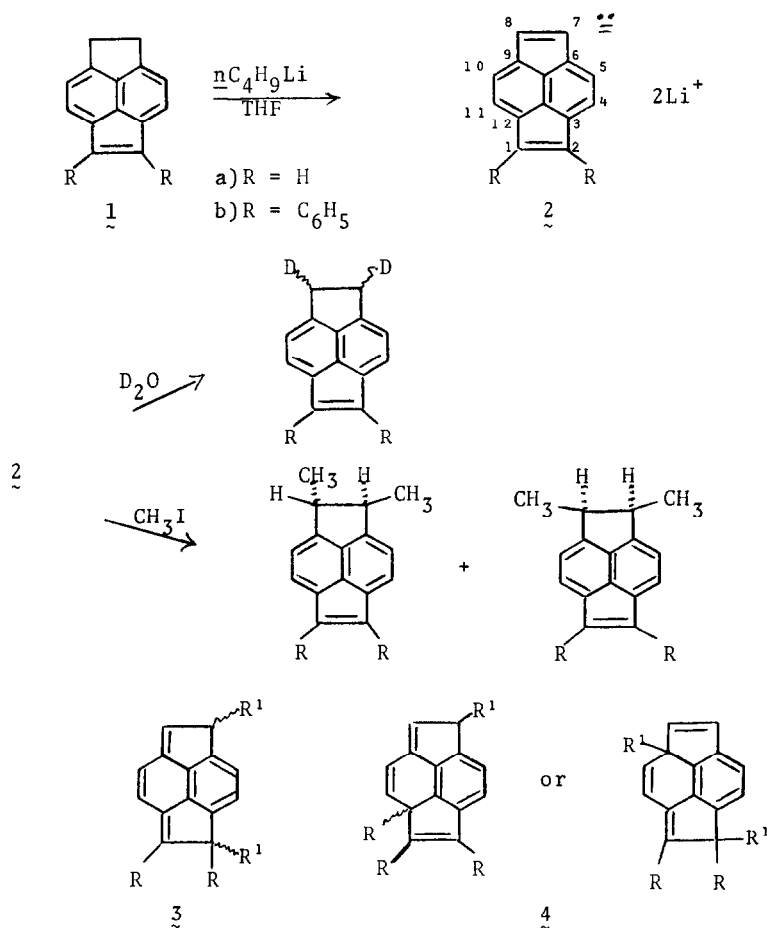
Madison, Wisconsin 53706

The generation of dianions from polycyclic unsaturated molecules normally entails two electron reduction.[2] Only recently has such species been generated by deprotonation of dihydropolycyclic unsaturated species-- most interestingly from 1,2-dihydro isomers.[3,4] In order to gain further insight into the electronic structure of the pyracylenes, we examined the behavior of dihydropyracylene towards strong metalating agents.[5,6] If the periphery electronic model is correct, deprotonation to the perturbed 14π electron aromatic dianion should be facilitated.[7]

1,2-Diphenyl-5,6-dihydropyracylene (1b)[6] in tetrahydrofuran was added to a -78° tetrahydrofuran solution of n-butyllithium (with or without N,N,N',N'-tetramethylethylenediamine). A deep red solution formed. Inverse quenching into a deuterium oxide solvent containing 2M deuteroacetic acid caused immediate reformation of the orange color of the dihydropyracylene (82% recovery, mp 218-9°). Examination by nmr and mass spectroscopy revealed 82.8% d_2, 15.3% d_1, and 1.8% d_0 (see Scheme 1) with the deuterium located at positions 5 and 6 exclusively. Corroborative evidence for the dianion present in the red solution was obtained by adding this solution to neat methyl iodide. Preparative tlc led to the isolation of bright orange needles (mp 158-160°) in 36% yield. Mass spectroscopy revealed the formula as $C_{28}H_{20}$. Nmr spectroscopy revealed a sharp doublet at $\delta 7.84$ (2H, d, J = 6.8

Scheme 1.   Generation and Reactions of Pyracylene Dianions

$$\underline{n}C_4H_9Li \quad \xrightarrow{\quad} \quad THF$$

a) R = H

b) R = C_6H_5

$2Li^+$

$\underset{\sim}{1}$ $\underset{\sim}{2}$

$\underset{\sim}{2}$

$D_2O \nearrow$

$\xrightarrow{\quad CH_3I \quad}$

+

or

$\underset{\sim}{3}$ $\underset{\sim}{4}$

Hz), 4.0 (0.34 H, q, J = 7 Hz), 3.43 (1.66 H, q, J = 7.0 Hz), 1.60 (5.0 H, d, J = 7.0 Hz), and 1.44 (1.0 H, d, J = 7.0 Hz) indicating the compound to be an approximately 1.6 mixture of the Z and E isomers of 5,6-dimethyl-1,2-diphenyl-5,6-dihydropyracylene.   Unfortunately, attempts to obtain the nmr spectrum of the dianion failed because of solubility problems.

Similar treatment of 1,2-dihydropyracylene ($\underset{\sim}{1a}$)[5a,6] led to a green solution which upon quenching led to recovered starting material (see Scheme 1). A similar solution could be generated by reducing pyracylene with sodium

naphthalenide in tetrahydrofuran.   In this case, quenching of the solution by
inverse addition into deuterium oxide generated 1,2-dideutero-1,2-dihydro-
pyracylene.   The mass spectrum at 12 ev indicated 77% d_2, 19% d_1, and 4% d_o.
The nmr spectrum which showed the signal intensity for the benzylic protons
($\delta 3.33$) to equal that of the ethylenic protons ($\delta 7.0$) and to equal 1/2 that of
the naphthalene AB quartet ($\delta 7.42$) located the deuterium at positions 1 and 2.
An nmr spectrum of the dianion solution (generated from 1a and n-butyllithium)
revealed two singlets of approximately equal intensity at $\delta 6.00$ and 6.75.
Utilizing the empirical relationship developed for peripheral 14π electron
dianions predicts chemical shifts of $\delta 6.00$ and 6.62 in excellent accord with
the experimentally determined values.[8]

In marked contrast to acenaphthalene dianion,[3] pyracylene dianions under-
go exclusive reaction at the ethylene bridge carbons.   The above quenchings
conclusively rule out the initial formation of either 1,5 or 1,8 addition
products such as 3 or 4.   Such an observation is in agreement with the idea
that these dianions are best represented as 14π electron dianions perturbed by
an internal vinyl crosslink.   Subsequent reaction then occurs at the site of
highest electron density (see Table 1).   Both Hückel and SCF-PPP[9]
calculations suggest all the negative charge resides on the peripheral carbon
atoms.   The excellent accord of the charge densities obtained from the nmr

Table 1.   Charge Distribution in Pyracylene Anions

	Position			
Dianion	1,2	4,11	5,10	7,8
2a[a]	1.208	1.084	1.084	1.208
2a[b]	1.262	1.135	1.135	1.262
2a[c]	1.21	1.08	1.08	1.21
2b[a]	1.207	1.084	1.083	1.208

a) Hückel charge densities. b) SCF-PPP π charge densities. c) Experimental
charge densities.

chemical shifts[10] with the theoretically calculated ones and, more strikingly, the excellent accord of the nmr parameters with those found for other 14π electron dianions whose charge is restricted to the periphery confirms the earlier description of the pyracylene system on the basis of the periphery electronic model.

References

1. Camille and Henry Dreyfus Teacher-Scholar Grant Recipient.

2. See for example, T. J. Katz, J. Amer. Chem. Soc., 82, 3784, 3785 (1960); ibid, 91, 1534 (1969); J.F.M. Oth, G. Anthoine, and J. M. Gilles, Tetrahedron Letters, 6265 (1968).

3. L. D. Kershner, J. M. Gaidis, and H. H. Freedman, J. Amer. Chem. Soc., 94, 985 (1972); C. V. Ristagno and R. G. Lawler, Tetrahedron Lett, 159 (1973); T. S. Cantrell, ibid, 1803 (1973).

4. a) J. J. Brooks, W. Rhine, and G. D. Stucky, ibid., 94, 7346 (1972); b) R. G. Harvey, L. Nazareno, and H. Cho, ibid., 95, 2376 (1973).

5. a) A. G. Anderson, Jr. and R. G. Anderson, J. Org. Chem., 23, 517 (1958); b) H. J. Richter and W. C. Feist, ibid., 25, 356 (1960).

6. B. M. Trost, G. M. Bright, C. Frihart, and D. Brittelli, J. Amer. Chem. Soc., 93, 737 (1971).

7. For some [12] annulene dianions see a) T. J. Katz and J. Schulman, ibid, 86, 3169 (1964); b) P. J. Garratt, N. E. Rowland and F. Sondheimer, Tetrahedron, 27, 3157 (1970); c) K. Hafner, Angew. Chem. Internat. Ed., 3, 165 (1964); d) [12] Annulene dianion has also been made by J.F.M. Oth, see footnote in ref 7b.

8. B. M. Trost and P. L. Kinson, J. Amer. Chem. Soc., 92, 2591 (1970).

9. D. H. Lo and M. A. Whitehead, Chem. Commun., 771 (1968).

10. T. Schaefer and W. G. Schneider, Can. J. Chem., 41, 966 (1963).