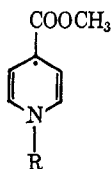


Additional Pyridinyl Diradicals. Intramolecular Association

Sir:

Four criteria guide our interpretation of the behavior of pyridinyl radicals: (a) the epr spectrum in solution; (b) the epr spectrum in a glass; (c) the epr signal strength (either in solution or in a glass); and (d) the nature of the visible absorption spectrum. The pyridinyl radicals **1** exhibit (a) well-resolved hyperfine



1, R = CH₃, CH₃CH₂, (CH₃)₂CH

epr spectra in dilute solution,^{1,2} (b) epr spectra with relatively little structure in a 2-methyltetrahydrofuran (MTHF) glass at 77°K;³ (c) an epr signal strength much lower than that expected as the concentration of **1** is raised or the temperature of the solution is lowered; and (d) an intense visible absorption band at high concentrations or low temperatures.⁴ The latter two re-

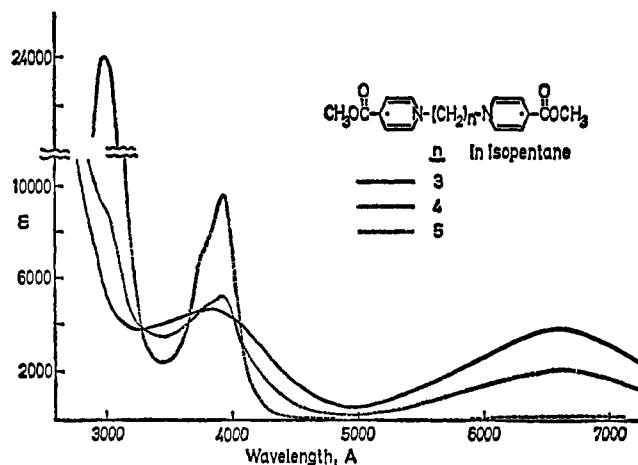


Figure 1. The absorption spectra of the pyridinyl diradicals in isopentane solution. The pyridinyl radicals are separated by varying numbers of methylene groups, e.g., (CH₂)₃ in **3**, (CH₂)₄ in **4**, and (CH₂)₅ in **5**.

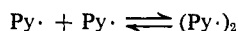
We now report remarkable differences in the behavior of the pyridinyl diradicals **3**, **4**, and **5** which are compared with **2** in Table I. The diradicals are pre-

Table I. Behavior of Pyridinyl Diradicals

Criterion	2	3	4	5
Solution	hfs, concd ^{a,d}	mfs, concd ^{b,e}	hfs, concd ^e	hfs, dilute ^e
Epr	Broad, dilute	Broad, dilute	and dilute	
MTHF ^d glass 77°K (dilute)	Triplet	Monoradical	Monoradical	Monoradical
Epr signal strength ^{e,f}	Expected	1%	20%	Expected
Visible absorption, 25°	Moderate intensity	Strong	Strong	Very weak
ε _{max} in 6000-7000-A region ^e	820 ^d	3800	2060	<100

^a hfs = hyperfine structure. ^b mfs = medium fine structure. ^c Radical concentration measured by reaction with methyl viologen; spin concentration by comparison of the area of epr absorption curves with that of a standard (**1**, R = CH₃). ^d 2-Methyltetrahydrofuran. ^e Isopentane. ^f Of isopentane solution.

sults arise from the formation of a singlet (diamagnetic) diradical dimer which has a strong charge-transfer transition in the visible region^{4,5} (**1** = Py·).



The pyridinyl diradical **2** had (a) a broadened epr spectrum with little structure in solution; (b) a characteristic triplet epr spectrum in MTHF glass; (c) an epr signal strength which decreased with concentration; and (d) a visible band of only moderate intensity in dilute solution.⁶

(1) E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **86**, 5515 (1964).

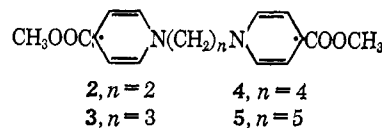
(2) M. Itoh and S. Nagakura, *Bull. Chem. Soc. Japan*, **39**, 369 (1966).

(3) E. M. Kosower and H. P. Waits, 148th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965. At very high radical concentrations, the epr spectrum has "wings" separated by 83 gauss which may be due to a small amount of triplet diradical dimer.

(4) M. Itoh and S. Nagakura, *Tetrahedron Letters*, 227 (1966).

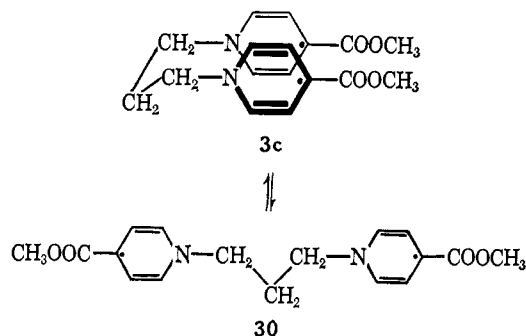
(5) M. Itoh and S. Nagakura, *J. Am. Chem. Soc.*, in press.

pared by reduction of the corresponding pyridinium diiodides in the manner previously described,⁶ except that isopentane was used as the extractant.



The low-spin concentration of **3** (and the lack of an observable triplet) suggests that **3** is present in closed (**3c**) and open (**3o**) forms. Increased hyperfine structure in the epr spectrum of **3** at higher concentrations in solution indicates that **3o** can dimerize (or polymerize) like **2** (which is completely in the **2o** form⁶). The diradical **4** has a higher proportion of the open form than **3**, and apparently only the **5o** form is present in solutions of the diradical **5**. Visible absorption intensities are in accord with these conclusions (see Figure 1).

(6) E. M. Kosower and Y. Ikegami, *ibid.*, **89**, 461 (1967).



These findings extend our knowledge of the behavior of diradicals and of the phenomenon of radical-radical association to diradical dimers.³⁻¹⁰

Acknowledgment. The authors are grateful to Dr. P. C. Huang for the preparation of the pyridinium diiodides and to the National Institutes of Health, the National Science Foundation, the Army Research Office (Durham), and the Research Laboratories, Edgewood Arsenal (through Contract DA 18-035-AMC-138(A)), for support.

(7) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

(8) E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5524 (1964).

(9) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2538 (1964).

(10) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

(11) On leave from the Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Tokyo, Japan.

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Direct Observation of a Homoaromatic Bishomocyclopentadienide Anion¹

Sir:

Bicyclooctadiene II has been reported by Brown and Ocolowitz² to be more reactive than monoene I in allylic proton-deuterium exchange by a factor of $10^{4.5}$ in DMSO-KOBU-*t* at 50°. This increased reactivity of the diene was ascribed to the presence of the additional olefinic group in II, and the possible formulation of the intermediate anion as a bishomocyclopentadienide species III was suggested. The reported exchange involved only allylic protons, and no formation of isomeric tricyclic and tetracyclic hydrocarbons IV and V from the diene II was observed.

HMO calculations do in fact predict a bonding interaction between allylic anion and olefinic systems in a carbanion such as IIIa. Such interaction is predicted to be quite appreciable³ even for (β_{27}/β_0) equal to 0.3, and it is specifically allowed for by the 1,3-bishomocyclopentadienide⁴ description III. The charge

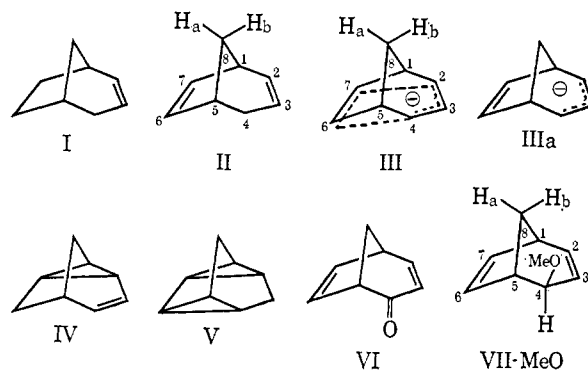
(1) (a) Research supported in part by the U. S. Army Research Office (Durham); (b) research supported in part by the National Science Foundation; (c) acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) J. M. Brown and J. L. Ocolowitz, *Chem. Commun.*, 376 (1965).

(3) Simple HMO calculations give values of $E_\pi - 6\alpha$ of $4.828\beta_0$, $5.032\beta_0$, $5.346\beta_0$, and $5.862\beta_0$ for β_{27}/β_0 values of 0, 0.3, 0.5, and 0.75, respectively. The corresponding negative charges at $C_{3,1}$: $C_{6,7}$: C_3 are 0.426:0.064:0.021, 0.346:0.126:0.056, and 0.263:0.177:0.120 for β_{27}/β_0 values of 0.3, 0.5, and 0.75, respectively.

(4) (a) S. Winstein, *J. Am. Chem. Soc.*, **81**, 6524 (1959); S. Winstein

distribution in such an ion depends, of course, on the molecular geometry and the relative importance of the different atomic orbital overlaps.³ One may visualize protonation at the different carbanionic centers of III, C_2 or C_4 to yield bicyclic diene II, C_6 or C_7 to yield tricyclic IV, and C_3 to give tetracyclic V. One may in fact anticipate the possibility of base-catalyzed equilibration of II, IV, and V, and such is indeed observed^{4c,5a} in Streitwieser's catalyst-solvent system,^{5b} $CsNHC_6H_{11}$ in $C_6H_{11}NH_2$, which gives much greater equilibration (and exchange) rates than does the KOBU-*t*-DMSO system. We are now able to report the direct observation of anion III and its behavior in protonation since relatively stable solutions of anion III in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) may be prepared by the classical ether cleavage method^{6a} using the reaction between Na-K alloy and *exo*-4-methoxybicyclo[3.2.1]octadiene-2,6 (VII-OMe).⁷



Ether VII-OMe was prepared by methylation of the corresponding *exo* alcohol⁷ VII-OH, mp 45-48°, *p*-nitrobenzoate⁷ mp 79-81°. Alcohol VII-OH was obtained along with its *endo* epimer,⁷ *p*-nitrobenzoate⁷ mp 72-72.5°, by various reductions of the corresponding ketone^{8a} VI; it was also obtained by saponification of the benzoate ester from *t*-butyl perbenzoate oxidation of diene II. The nmr spectrum of VII-OMe as well as that of diene^{8b} is summarized in Table I.

On shaking in THF or DME with Na-K alloy at ca. 0°, VII-OMe reacts quite rapidly to generate the bicyclooctadienide salt.^{6b,c} This reaction was carried out in an evacuated apparatus which permitted filtration to remove excess alloy and methoxide salt and collection and concentration of the carbanion solution in an nmr tube. The resulting orange carbanion solutions are only very faintly contaminated, e.g., with diene II, and are stable for many hours. One of the signals in the nmr spectrum of III is obscured by a solvent

and J. Sonnenberg, *ibid.*, **83**, 3244 (1961); (c) S. Winstein, Chemical Society International Symposium on Aromaticity, Sheffield, England, July 6-8, 1966; Special Publication No. 21, The Chemical Society, London, 1967.

(5) (a) J. M. Nicholson, unpublished work; (b) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).

(6) (a) K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924). (b) Attempts to generate anion III by reaction of Na or Na-K alloy with diene II or tricyclic bromide^{4c} in THF were not very successful. (c) J. M. Brown (private communication) has also employed this method to generate III.

(7) New compounds gave satisfactory carbon and hydrogen analyses. Configurations assigned on the basis of the usual nmr and chemical criteria.

(8) (a) P. K. Freeman and D. G. Kuper, *Chem. Ind. (London)*, 424 (1965); (b) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).