Substituent Effect on the Electrochemical Oxidation of Arylmethyl Anions. 4. Effect of Pyridine Rings

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Electrochemical oxidation of the lithium anions of isomeric benzylpyridines and pyridyldiphenylmethanes was examined by cyclic and differential pulse voltammetry in tetrahydrofuran solution. The oxidation processes are dependent on the nitrogen position and anion stability. The products of the electrochemical oxidations were characterized and compared with a related homogenous oxidation. The NMR spectra of the lithiapyridyldiphenylmethanes are recorded and their pK values were determined by NMR competition experiments. The electrochemical oxidations and the acidity data for diarylmethyl and triarylmethyl anions are compared.

Electrochemical methods have provided valuable information about reactive anions and cations.[1-3] With use of the thermodynamic cycle indicated in reactions 1 to 3,

$$\text{R–H} \rightarrow \text{R}^\bullet + \text{H}^\bullet \quad (1)$$

$$\text{R}^\bullet + \text{e} \rightarrow \text{R}^- \quad (2)$$

$$\text{H}^\bullet \rightarrow \text{H}^+ + \text{e} \quad (3)$$

relationships between bond energies, oxidation potentials, and acidities have been studied.[1] For a series of organic anions, the ionization potential of the hydrogen atom term remains the same and can therefore be treated as a constant term. This leads to eq 4 for the interelation among these three terms.

$$\text{p}K = \text{BDE}/1.398 + E_{1/2}/0.059 + C \quad (4)$$

Determination of these several terms is often very difficult for highly reactive anions, but they are fundamental to reactivity–structure relationships and very useful for understanding reactivity patterns. Therefore, electrochemistry has been a particularly valuable method when only one term (usually pK)[4] has been determined and for comparing values obtained by other methods.

In previous work we have investigated the electrochemical oxidation of diaryl-[3a] and triarylmethyl anions[3b] and the effects of electron-donating and -withdrawing groups. In general, parallel effects are observed, but there are important differences due to the differing geometries of the two anionic systems.[5] For the triarylmethyl species the propeller geometry of the aryl rings leads to reversible one-electron oxidations and nonlinear sequential substituent effects.[3b] For the diarylmethyl species, the essentially planar geometry of the aryl rings leads to irreversible one-electron oxidations. Substituent effects are greatest when this geometry is disturbed.[3a] In spite of the large geometric differences in diphenylmethyl and triphenylmethyl anions, the pK values and E_{oxid} are suprisingly very similar.

We have now investigated the effect of larger changes in the nature of the carbanions by the introduction of a single nitrogen atom in the 2, 3, or 4 position of an aryl ring in each anions series. This substitution provided major changes in anion stabilities, ion pairing, aggregation, and electron density distributions.[6]

Comparison of anions with reversible oxidations presents no great difficulties, but for irreversible processes both the theoretical and practical aspects are problematical. In cyclic voltammetry (CV) for a reversible electrode process the half-wave potential is equal to the voltammetric standard potential. The half-wave potential is taken as the average of the potentials at the cathodic and anodic current maxima. For irreversible electrode processes only one potential maximum is observed, and the relationship to the reversible potential involves kinetic as well as thermodynamic terms. Kochi has noted that for closely related systems the kinetic components are similar and the irreversible potentials are very close to the actual reversible potentials.[7] Nevertheless some ambiguity is involved in the assignment of the voltage maximum to what is sometimes a broadened voltammogram. This problem can be alleviated by using differential pulse voltammetry (DPV). In CV the potential excitation is triangular with respect to time whereas in DPV the potential excitation is a pulse superimposed on a linear ramp. For irreversible electrode processes DPV offers advantages resulting from the more symmetrical and narrower voltammogram.

In previous studies we noted a relationship between the acidities of the parent compounds and the oxidation potentials of the anions.[3] Although the pK values for the benzylpyridines are known,[8] the pK values for the comparable pyridyldiphenylmethanes are not available. These were obtained by NMR methods in the present study and the values are compared with those for similarly substituted arylmethyl and diarylmethyl anions.

Results and Discussion

The anions were prepared from the hydrogen precursors, diphenylmethane, benzylpyridines, triphenylmethane, and pyridyldiphenylmethanes by reaction with butyllithium in tetrahydrofuran (THF). The details of anion preparation and transfer to the electroanalytical cell are described in the Experimental Section. Each oxidation was monitored by the addition of anthracene, which serves as an internal standard by virture of the known one-electron reversible process.

Controls for DPV were established by comparing the CV and DPV for the well-known reversible and irreversible processes of the triphenylmethyl and diphenylmethyl anions, respectively. Figure 1 depicts the cyclic and differ-

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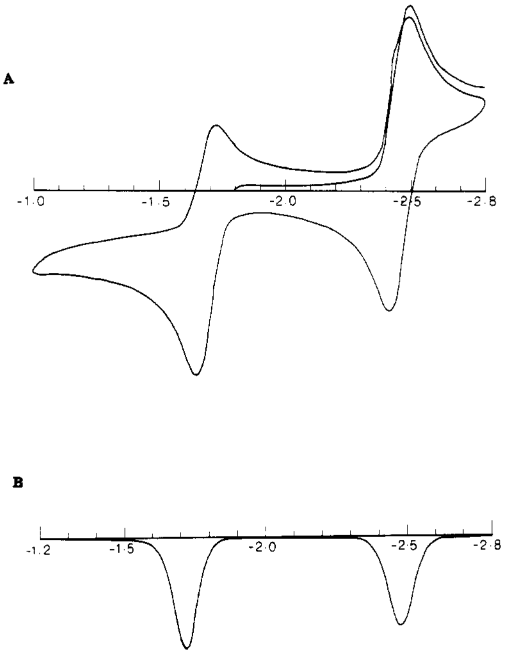


Figure 1. Voltammograms for (triphenylmethyl)lithium and anthracene in THF solution: (A) cyclic voltammogram from −2800 to −800 mV at a scan rate of 500 mV/s; (B) differential pulse voltammogram from −2800 to −1000 mV of the same solution at a scan rate of 4mV/s. See text for additional details.

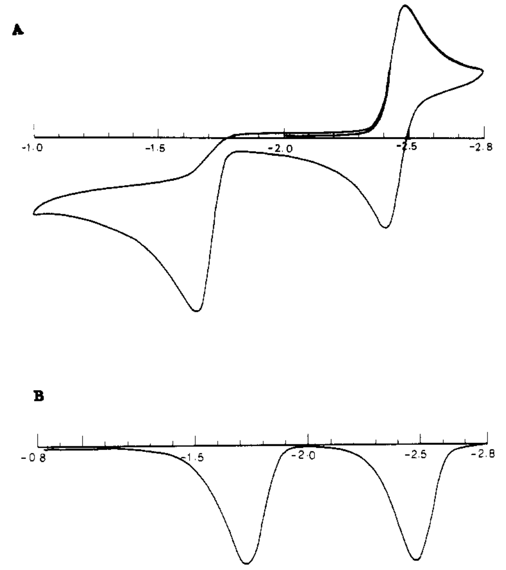


Figure 2. Voltammograms for (diphenylmethyl)lithium and anthracene in THF solution: (A) cyclic voltammogram from −2800 to −800 mV at a scan rate of 500 mV/s; (B) differential pulse voltammogram from −2800 to −1000 mV of the same solution at a scan rate of 4mV/s. See text for additional details.

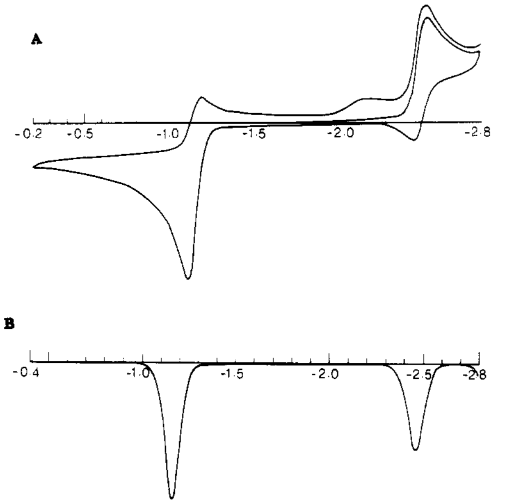


Figure 3. Voltammograms for lithio-4-pyridyldiphenylmethane and anthracene in THF solution: (A) cyclic voltammogram from −2800 to −200 mV at a scan rate of 500 mV/s; (B) differential pulse voltammogram from −2800 to −400 mV of the same solution at a scan rate of 4mV/s. See text for additional details.

ential pulse voltammograms of the triphenylmethyl anion. The more negative process in both is the reversible anthracene reduction at −2.05 V. For the CV the half-wave potentials are derived from the somewhat broadened but easily measured anodic and cathodic current maxima. The DPV curves (Figure 1b) are significantly more symmetrical and somewhat narrower ($W_{1/2}$ = 100 mV). The related voltammograms for the diphenylmethyl anion depicted in Figure 2 reveal the anodic maximum for the anion in the CV similar in shape to the triphenylmethyl anion but without the cathodic maximum. On the other hand the DPV for this anion is more similar in detail to the DPV for the triphenylmethyl anion. The peak width at half height (200 mV), while greater than that of the triphenylmethyl anion, is considerably less than the approximately 350 mV width of the CV curve. Additionally, the curve is far more symmetrical, and therefore the current maxima are determined with greater facility. A measure of the precision of the methods was obtained from multiple determinations of different samples. The values for the potentials and standard deviations (in parentheses) for CV and DPV for the triphenylmethyl anion are −1.290 (±0.002) and −1.263 (±0.002) V vs. Ag/AgCl. The first value is the $E_{1/2}$ and the second value is $E_{1/2} + \Delta E/2$ where ΔE is the pulse voltage. Since ΔE is 50 mV the agreement is that expected for a reversible process. For the diphenylmethyl anion the CV and DPV values are −1.250 (±0.007) and −1.294 (±0.004) vs. Ag/AgCl. For the irreversible process the CV value correspond to the E_p, and the DPV value is as before $E_{1/2} + \Delta E/2$. Since $E_p = E_{1/2} + 28$ mV the values should be essentially the same. The difference and the reproducibility differences are characteristics of the method. Thus DPV offers no advantage in precision for the reversible process but improved precision for the irreversible process.

The cyclic voltammogram of the 4-benzylpyridine anion reveals a reversible electrode process for anthracene at −2.050 V and an irreversible oxidation at −0.639 V. The DPV for the same solution leads to related values, albeit with less ambiguity in the assignment for the value for the irreversible process (see paragraph at the end of paper about supplementary material). The electrode process is very similar to that of the diphenylmethyl anion and the oxidation potential is 0.611 V less.

As expected the anions with three rings exhibited different oxidative behavior from the two ring systems. The electrochemical behavior of the 4-pyridyldiphenylmethyl anion depicted in Figure 3 reveals a quasi-reversible oxidation at −0.707 ± 0.004 V. In spite of the lack of full reversibility, the degree of reproducibility is the same as for the fully reversible anthracene and triphenylmethyl anions. The DPV curves are similar and the values from CV and DPV agree well.

Table I records the CV and DPV data for all of the anions. The position of the nitrogen atom in the aromatic ring has a marked effect on the oxidation potential in the order 4 > 2 > 3. The magnitude of the effect is similar for both ring systems with average Δ values of 0.548, 0.335,

Table I. Cyclic and Differential Pulse Voltammetric Data for Lithium Anions of Diphenylmethane, Benzylpyridines, Triphenylmethane, and Pyridyldiphenylmethanes

lithium anion[a]	E^b	E^c	p/p^d	$I_a/I_c{}^e$	E^f	E^g	$W_{1/2}{}^h$
diphenylmethane	1700 ± 7	1250 ± 7		0.0	1744 ± 4	1294 ± 4	200
3-benzylpyridine	1420 ± 8	970 ± 8		0.0	1497 ± 4	1047 ± 4	125
2-benzylpyridine	1274 ± 10	822 ± 10		0.0	1421 ± 4	971 ± 4	150
4-benzylpyridine	1089 ± 10	639 ± 10		0.0	1192 ± 4	742 ± 4	200
triphenylmethane	1740 ± 2	1290 ± 2	65	0.68	1713 ± 2	1263 ± 2	100
3-pyridyldiphenylmethane	1505 ± 5	1055 ± 5	174	0.25	1489 ± 3	1039 ± 3	100
2-pyridyldiphenylmethane	1372 ± 4	922 ± 4	189	0.24	1367 ± 3	917 ± 3	110
4-pyridyldiphenylmethane	1194 ± 3	744 ± 3	110	0.36	1170 ± 3	720 ± 3	90
anthracene	2500 ± 2	2050 ± 2	63	0.85	2479 ± 2	2029 ± 2	100

[a] The solvent is THF and the supporting electrolyte is lithium perchlorate. The reference electrode is Ag/0.1 M silver nitrate in acetonitrile. [b] Potential vs. Ag/$AgNO_3$ (mV) at the anodic peak current maxima for the diaryl compounds and half-wave potential for the triaryl compounds. [c] Potential (mV) vs. Ag/AgCl reference electrode.[3] [d] Peak potential separation for anodic and cathodic current maxima. [e] Current ratio for cathodic and anodic processes. [f] DPV voltammetric peak potential vs. Ag/$AgNO_3$ (mV) at maximum for anodic process (E_p). [g] Potential vs. Ag/AgCl reference electrode (mV). [h] Line width at half-height in mV.

Table II. ^{1}H NMR Chemical Shifts for the Pyridyldiphenylmethanes, Triphenylmethane, and the Lithium Salts[a]

		lithium compound		
atom[b]	triphenylmethane	4-pyridyldiphenylmethyl	3-pyridyldiphenylmethyl	2-pyridyldiphenylmethyl
α				
	5.41	5.18	5.23	
o	7.37	7.26	7.35	7.35
	7.06	6.92	6.93	7.20
m	6.57	6.94	6.77	6.91
	7.06	7.08	7.06	7.09
p	6.03	6.63	6.36	6.53
	7.06	7.04	7.01	7.01
2		6.46	7.38	6.60
		6.71	7.05	6.84
3		6.75	6.25	6.41
		8.40	6.64	6.99
4			6.45	5.48
			8.34	6.56
5		6.75		7.14
		8.40		8.43
6		6.46	7.99	
		6.71	8.49	

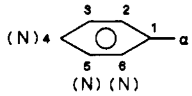
[a] The upper number is the shift for the anion (0.4 M in 80% THF/20% C_6D_6) and the lower number is the shift for the neutral species in C_6D_6. Shifts are recorded in ppm relative to internal Me_4Si. [b] The numbering system is the same as that used in Table III.

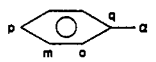
and 0.235 V from the corresponding all-carbon systems. These differences mirror the known differences in anion stabilities of the benzylpyridines and suggests similar trends for the acidity of the pyridyldiphenylmethanes. As indicated previously, p*K* values for the pyridyldiphenylmethanes were not available and these were obtained by NMR methods.

Determination of anion equilibria by NMR requires the evaluation of the concentrations of anions and precursors. Initially the spectrum of each species is assigned independently. The success of the method depends in large measure on regions of the spectra where each species has unique absorptions. Tables II and III record the proton and carbon-13 shift data for the pyridyldiphenylmethanes and their lithium salts in THF solution.

Heterocorrelated 2-D proton–carbon NMR spectra proved valuable in providing assignments. The charges in the several rings and at the nitrogen atoms were calculated from the relationship between ^{13}C chemical shift and charge (160 ppm/e)[9] as described in related work with the benzylpyridines.[6] The charges in the pyridyl rings for lithio-3-pyridyl-, lithio-2-pyridyl-, and lithio-4-pyridyldiphenylmethane are 0.494, 0.606, and 0.729, respectively. As expected, the amount of charge in the pyridyl ring is dependent on the position of the nitrogen atom and is in the order 4 > 2 > 3.

Table III. ^{13}C NMR Chemical Shifts of Pyridyldiphenylmethanes, Triphenylmethane, and the Lithium Salts[a]





		lithium compound		
atom	triphenylmethane	4-pyridyldiphenylmethyl	3-pyridyldiphenylmethyl	2-pyridyldiphenylmethyl
α	90.4	97.8	89.6	95.2
	57.2	56.4	54.6	59.9
q	149.8	149.2	149.6	149.0
	144.4	142.6	143.2	143.6
o	124.0	130.0	126.7	127.8
	128.5	129.6	129.6	129.8
m	128.0	128.0	128.4	129.1
	129.9	128.7	128.7	128.5
p	113.1	120.5	117.5	119.4
	126.5	126.9	126.8	126.5
1		142.4	143.4	159.6
		152.4	139.5	163.6
2		110.2	122.8	117.7
		124.6	136.4	123.7
3		145.1	124.6	133.3
		150.2	123.2	135.9
4			125.9	104.5
			147.9	121.2
5		145.1		147.2
		150.2		149.7
6		110.2	142.3	
		124.6	151.2	

[a] The upper number is the shift for the anion (0.4 M in 80% THF/20% C_6D_6) and the lower number is the shift for the neutral species in C_6D_6. Shifts are recorded in ppm relative to internal Me_4Si.

The p*K* values for the pyridyldiphenylmethanes were measured by competition. In each system solutions of anions of known acidity were mixed with the pyridyldiphenylmethane to yield spectra where the concentrations of the several anions and the precursors could be measured. Reference acids were available from the work of Fraser.[8] The details and representative spectra are described in the Experimental Section. The p*K* values are compared with those for the benzylpyridines, diphenylmethane, and triphenylmethane in Table IV.

Figure 4 depicts the relationship between the change in acidity brought about by the introduction of a nitrogen

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(9) O'Brien, D. H., in ref 4, Ch. 7.

Table IV. Equilibrium Acidities of Picolines, Benzylpyridines, and Pyridyldiphenylmethanes

compound	p*K*	p*K*, corr.[a]	Δ[b]
toluene[c]	40.4	40.9	0
2-picoline[d]	34.0	34.5	6.4
3-picoline[d]	37.7	38.2	3.7
4-picoline[d]	32.2	32.7	8.2
diphenylmethane[e]	33.1	33.4	0
2-benzylpyridine[f]	28.3	28.6	5.1
3-benzylpyridine[f]	30.1	30.4	3.3
4-benzylpyridine[f]	25.2	25.5	8.2
triphenylmethane[e]	31.4	31.4	0
2-pyridyldiphenylmethane	27.5	27.5	3.9
3-pyridyldiphenylmethane	28.4	28.4	3.0
4-pyridyldiphenylmethane	23.3	23.3	8.1

[a] Statistical correction for number of hydrogens. [b] The difference in p*K* units between the N-substituted compound and the corresponding all-carbon analogue. [c] The value for toluene is an estimate and the generally accepted value (ref 10) is used. [d] See ref 8 and references cited therein. [e] Reference 4. [f] Reference 8.

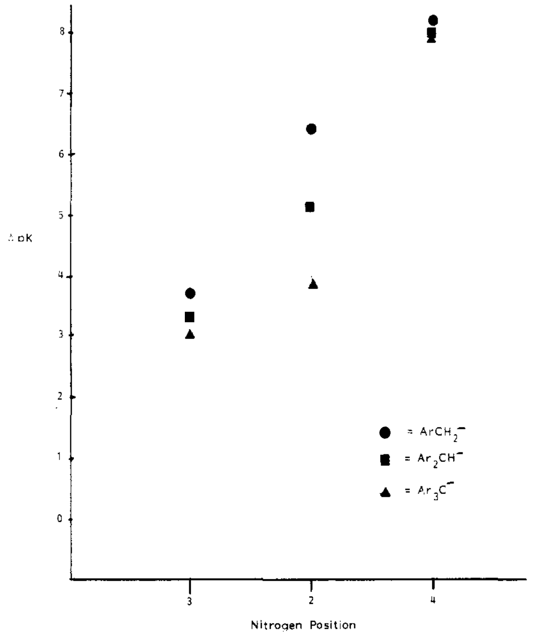

Figure 4. Change in p*K* brought about by nitrogen atom substitution in an aryl ring of arylmethyl anions with one, two, and three rings vs. position of nitrogen substitution.

Table V. Oxidative Dimerization of Diarylmethyl Anions by Electrochemical and Homogeneous Paths[a]

anion	yield, %	current yield,[b] %	diastereo-selectivity[c]	overpo-tential[e]
diphenylmethane	50	80		2.5
	d			
2-benzylpyridine	70	80	1.2/1.0	2.3
	70		1.2/1.0	
3-benzylpyridine	100	80	1.6/1.0	1.4
	50		1.0/1.4	
4-benzylpyridine	20	30	10.0/1.0	1.6
	75		1.0/1.0	

[a] The upper numbers are for the electrochemical dimerization and the lower numbers are for the solution dimerization using methanesulfonyl chloride (see text). [b] Current yield is based on the amount of charge passed. [c] Diastereoselectivity is for racemic/meso and is based on integration of the proton NMR signals of the α hydrogens of the different diastereomers. [d] Homogeneous reaction with lithiodiphenylmethane was not effected under these conditions (see text). [e] Overpotential in volts.

atom at the numbered position for the one, two, and three aryl ring systems. In each case the respective carbocyclic analogue is used as a basis for comparison. Two features are noted. First, the effect on a 4-nitrogen atom is the same within experimental error in each ring system. Second, the effect of a 2-substituted nitrogen atom decreases considerably with the number of rings. A reasonable explanation for the substituent pattern is a steric effect. Classically, the ortho (or 2) position is far more subject to steric effects, and many deviations from expected electronic effects have been assigned to these terms.[10] Additionally, for these lithium anions, previous work has shown that there is a close connection between the lithium and the nitrogen atom, and particularly large steric effects may be involved.[6] Finally this could be related to the observed inability to form an arylmethyl anion when all three rings have a nitrogen in the 2-position.[11]

From known p*K* values and oxidation potentials, eq 4 can be used to obtain values for the bond dissociation energies. This could give relative radical stabilities provided the heats of formation of the neutral species were either known or constant. In this set of isomeric molecules, it is likely that the enthalpies and entropies of formation of the neutral species are nearly equal. Moreover, similar solvation terms are expected for the neutral species. Accordingly, within this series differences in the energy terms associated with the initial state can be reasonably ignored.

In fact, within about 1 kcal/mol, the energies for the isomeric radicals are the same. This comes about because the differences in the acidities expressed in kcal/mol for the 3- and 2-benzylpyridines relative to 4-benzylpyridine of 6.7 and 4.3 are very similar to the corresponding oxidation potential differences of 6.0 and 5.3, respectively. A similar treatment for the pyridyldiphenylmethanes leads to the same conclusion. These conclusions can be compared with studies of the isomeric picolinyl radicals where similar absolute energies for the isomers have been determined.[12] Additionally, the bond dissociation energies for 2- and 4-benzylpyridines are found to be similar.[13] The nitrogen atom strongly stabilizes the anion but has little effect on the stability of radicals.[14]

In previous electrochemical studies of anion oxidation, the product was assumed to be the dimer but was not isolated.[1] Synthetic scale homogeneous and electrochemical oxidations of the diarylmethyl anions were studied to confirm the accepted scheme and to provide comparison with chemical oxidation. Homogeneous oxidation utilized methanesulfonyl chloride in diethyl ether.[15] Electrochemical oxidation employed a platinum electrode in THF with lithium perchlorate as the supporting electrolyte. Results are summarized in Table V. The isolation of 1,1,2,2-tetraphenylethane in substantial yield from the electrochemical oxidation of the diphenylmethyl anion demonstrates that the postulated scheme for the anion oxidation is correct. Unfortunately the comparison with chemical oxidation was precluded in this case as the anion was insoluble in diethyl ether and attempts to use THF for the homogeneous oxidation led to tars.

For the pyridyl compounds the products are the diastereomeric meso and the enantiomeric pair. NMR spectroscopy was used to determine the ratio of diaste-

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(10) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; p 130 ff.

(11) White, D. L.; Faller, J. W. *Inorg. Chem.* **1982**, *21*, 3119.

(12) Barton, B. D.; Stein, S. E. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1755.

(13) Rossi, M. J.; McMillan, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031.

(14) Ingold, K. U. In *Free Radicals*; Kochi, J., ed.; Wiley Interscience: New York; 1973; p 78 ff.

(15) Skattebol, L.; Boulette, B. *J. Organomet. Chem.* **1970**, *24*, 547.

reomers. From the ^1H and Hetcor spectra the methine protons are easily assigned at approximately 5 ppm. The mixtures had two singlets in the region separated by about 0.1 ppm. While the identity of each peak cannot be ascribed to the individual isomer, the ratio of singlets changed with repeated recrystallizations as the melting point approached that reported for the single isomer.[15]

The most interesting trend in the dimerization data is the change in diastereoselectivity in going from homogeneous to electrochemical oxidation. This suggests that the electrochemical dimerization occurs at least in part at the electrode surface before diffusion. The radicals would then be subject to the powerful forces at the double layer and the product composition could differ markedly from the dimerization in bulk solution. Since the forces at the double layer are electrical, it would be expected that the species of greater dipole moment would be affected more. In fact, the difference in diastereoselectivity is proportional to the dipole moment between the diastereomers. This is consistent with a dimerization at the strong electric field of the double layer. If the transition states for the dimerization reflect the diasteromeric products, then differing selectivities in the bulk solvent and the electrode double layer could lead to the observed results. Essentially, the homogeneous oxidation is not selective whereas variable and in some cases pronounced diastereoselectivities are noted for the electrochemical oxidation. In any event this simple procedure may offer attractive alternative means of preparing dimers in reasonable yields.

In the introduction the interelation of terms in the thermodynamic cycle was described in eq 4. This cycle, including oxidation potential, acidities, and bond dissociation energies for carbanions has received considerable attention. Recently, Bordwell and Bausch[2] have successfully correlated the bond dissociation energies of the acidic C–H bonds of the arylmethane type with the AOP (acidity–oxidation potential) values of a fluorenyl equivalent. The linearity of such a correlation confirms the soundness of the AOP thermodynamic cycle.

In the general case, when the bond dissociation energy, pK, and the oxidation potential have no additional relationships, then the AOP cycle is the simplest method for comparison. If there is a second relationship between the variables, however, then considerable simplification is possible. Within a series of related compounds bond dissociation energies may be similar and therefore oxidation potentials and pK values would be linearly related.

As discussed earlier this situation obtains for the isomeric benzylpyridines and the pyridyldiphenylmethanes. If the data for other diaryl- and triarylmethyl anions are included[3] in the comparison, some indication of the scope and limitations of the relationship can be determined. Figure 5 depicts the relationship between the oxidation potentials and the pK values of the diarylmethyl anions and triarylmethyl anions. For the eleven diaryl compounds a linear relationship with a correlation coefficient of 0.993 and a slope of −0.0779 is found. For the six triarylmethyl compounds, a line with a correlation coefficient of 0.980 and a slope of −0.742 is observed. Thus within the experimental error the slopes are the same and similar to slopes of −0.06 to −0.08 V per pK unit found in other carbanion systems.[16,17] However, the lines are displaced.

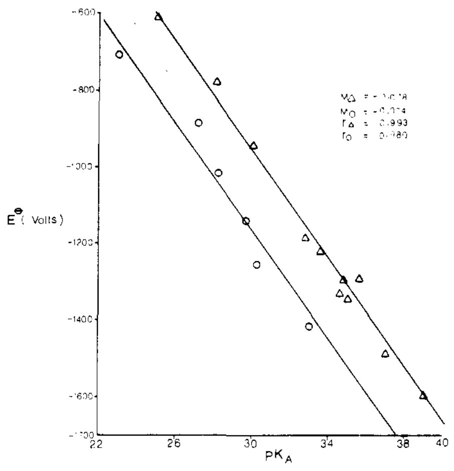

Figure 5. Relationship between oxidation potentials and equilibrium acidities for diarylmethyl (△) and triarylmethyl (○) anions.

The linear displacement of the diarylmethyl and triarylmethyl lines of 5.3 kcal/mol at a constant pK is equivalent to the difference in the bond dissociation energies of the two series. This value may be compared with the experimentally determined bond dissociation energy difference for diphenyl- and triphenylmethane of 6.4 kcal/mol.[13,18] This agreement provides additional confirmation to the idea that the compounds on the lines in the graph have similar bond dissociation energies.

Thus within a series of closely related anions where the conjugate acids have similar bond dissociation energies, the base strength and reduction potential are directly related. The choice of a stronger base also dictates a stronger reducing agent and the quantitative relationship from eq 4 is useful. However, for anions of different series, the relationship is more complex and a stronger base might not be a stronger reducing agent. For reactions with substrates having differing sensitivities to base strength and reduction potential, reaction rates might show these same trends.

In particular, some reactions with nucleophiles have both a one-electron and two-electron pathway. To a large degree the one-electron component should depend upon the reduction potential of the nucleophile whereas the two-electron pathway might be more sensitive to the base strength. With these series of known values for these anions, it should be possible to test and utilize reactivity patterns.

Experimental Section

The analytical electrochemistry was performed by using a BAS-100 electrochemical analyzer. The synthetic scale electrochemistry was performed on a BAS CP-2 potentiostat. The proton, carbon, and two-dimensional NMR spectra were recorded on a Varian XL-300 spectrometer. Chemical shifts are reported relative to 1% internal Me_4Si. Mass spectra were recorded on an AEI MS-902 high resolution electron impact mass spectrometer. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Diphenylmethane, triphenylmethane, the benzylpyridines, and the pyridyldiphenylmethanes were purchased from Aldrich and used directly. n-Butyllithium (2.6 M in hexane) and diisopropylamine were also obtained from Aldrich. Anhydrous lithium perchlorate (Aldrich) was stored in a desiccator. THF and diethyl ether were distilled from sodium benzophenone prior to use.

Anion Preparation. Anions were prepared on an Ace Glass No-Air inert gas delivery system. All glassware was oven-dried, assembled while hot, and then flame-dried, evacuated, and purged with argon three times before use. Stock solutions of the anions were prepared by reactions of lithium diisopropylamide and the heterocyclic compound as described previously[9] and were 0.2 M for electrochemistry and 0.5 M for NMR studies.

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Electroanalytical Cell. The cell was modified to include a fourth neck in a 25-mL round-bottom flask. The working, reference, and auxiliary electrodes occupied three ports and a pressure-equalizing dropping funnel occupied the remaining port. The working electrode consisted of a flat circular plug of platinum with a surface area of 0.1 mm^2. The platinum was sealed in glass and connected with mercury to a copper wire. The auxiliary electrode was identical except that the surface area of the platinum was 5.0 mm^2. The reference electrode consisted of a silver wire in 0.1 M silver nitrate in acetonitrile. The reference electrode was connected to the solution via a Vycor tip. Before use, the working and auxiliary electrodes were treated with concentrated nitric acid and polished with alumina. All three electrodes were washed in water and rinsed with acetone.

The glassware was oven-dried and assembled without the electrodes and was flame-dried under argon. To the four-neck flask was added 2.0 g (20 mmol) of anhydrous lithium perchlorate and 20 mg of anthracene (0.11 mmol). The electrodes were positioned and 20 mL of THF was syringed into the flask. A 0.2 M anion solution prepared under argon was transferred by syringe to the addition funnel. The entire apparatus was brought to the BSA-100 and after appropriate electrical connections the anion solution was slowly added to the four-neck flask to provide the anion in the desired concentration.

All standard potentials were measured by reference to the reversible one-electron reduction of anthracene. The scan range included the anthracene electrochemistry and thus the anthracene served as a internal absolute voltage standard and a diagnostic for reversibility. The concentration of the anion solution and the anthracene was approximately 4 mM. Under these conditions the peak current was 5.0 ± 1.0 μA. After quenching the anion, a background current of less than 1 μA due to electrode charging was found.

Typical conditions for cyclic voltammetry include a scan rate of 500 mV/s from −2800 to −600 mV with solution resistance of 9000 Ω and IR compensation. Each potential was measured 16 times. Typical conditions for differential pulse voltammetry include a scan rate of 4 mV/s from −2800 to −700 mV, a pulse width of 50 ms, a pulse period of 1 s with an amplitude of 50 mV, and a sample width of 17 μs. Each potential was measured eight or more times.

Electrosynthetic Cell Preparation. A 1-L Ace Glass electrosynthetic cell was used with a platinum mesh working electrode and a coil of copper wire for the auxiliary electrode. The reference electrode was Ag/AgCl in 3 M NaCl(aq) which was connected to the solution via a Vycor tip. Under argon, 10.0 g of lithium perchlorate was added to the main chamber and an additional 3.0 g was added to the auxiliary chamber. An amount of THF (120 mL) was added and magnetic stirring was begun. The entire apparatus was placed in an ice bath and 20 mL of a 0.4 M anion solution was added via syringe. In an alternate procedure the anion was generated in situ in the main chamber of the cell from the precursors.

The potential initially at 0.0 V was moved positively until a limiting current was observed. Initially current values of 200 mA were found and after 3 h the current was less than 5 mA. At the end of the electrosynthesis a small quantity of 2-propanol was added to the catholyte to react with the lithium produced by reduction of the supporting electrolyte. The anolyte from the auxiliary electrode was transferred to a 500-mL flask and water was added. THF was distilled and then ether was added. The product was filtered, washed, and dried.

1,1,2,2-Tetraphenylethane. Oxidation of the anion from 2.0 g (12.0 mmol) of diphenylmethane, followed by workup, yielded 1.0 g (6.0 mmol) of 1,1,2,2-tetraphenylethane (50% yield, 80% current yield), mp 212–214 °C (lit.[19] mp 214–215 °C). The proton and carbon NMR spectra were identical with those of a sample prepared by an alternate route. The mass spectrum gave the expected peaks.

1,2-Di-2-pyridyl-1,2-diphenylethane. Oxidation of the anion generated from 2.0 g (12 mmol) of 2-benzylpyridine yielded 1.4 g (8.4 mmol) of 1,2-di-2-pyridyl-1,2-diphenylethane (70% yield, 80% current yield). Physical and spectroscopic data are as follows: mp 242–244 °C dec (lit.[15] mp 240–241 °C); ^{1}H NMR ($CDCl_3$) δ 5.27, 5.29 (2 H, s), 6.8–7.5 (16 H, m), 8.4, 8.5 (2 H, d); ^{13}C NMR ($CDCl_3$) 57.5, 57.7, 120.8, 121.0, 123.9, 124.2, 126.0, 126.1, 128.0, 128.6, 128.8, 135.9, 136.0, 141.9, 142.1, 148.8, 149.1, 162.0, 162.5; mass spectrum *m/e* 336 (relative intensity) (21), 169 (37), 168 (100), 167 (64). This agrees well with the previously reported spectrum.[15] Diastereoselectivity was determined by the integration of the proton signals at 5.27 and 5.29 ppm.

1,2-Di-3-pyridyl-1,2-diphenylethane. Oxidation of the anion from 2.0 g (12.0 mmol) of 3-benzylpyridine followed by workup as above yielded 2.0 g (12.0 mmol) of 1,2-di-3-pyridyl-1,2-diphenylethane (100% overall yield, 80% current yield). Physical and spectroscopic data are as follows: mp 334–338 °C dec; ^{1}H NMR ($CDDl_3$) δ 4.78, 4.79 (2 H, s), 7.0–7.5 (14 H, m), 8.3, 8.4 (2 H, d), 8.5, 8.6 (2 H, d); ^{13}C NMR ($CDCl_3$) 53.6, 53.7, 123.2, 123.5, 126.6, 126.8, 128.3, 128.4, 128.6, 128.8, 135.5, 135.6, 138.3, 141.4, 141.5, 147.6, 150.1; mass spectrum, *m/e* (relative intensity) 336 (31), 169 (25), 168 (100), 167 (38), 115 (10); calcd for $C_{24}H_{20}N_2$ 336.1626, found 336.1640. Diastereoselectivity was determined by integration of the signals at 4.78 and 4.79 ppm.

1,2-Di-4-pyridyl-1,2-diphenylethane. Oxidation of the anion generated from 2.0 g (12.0 mmol) of 4-benzylpyridine followed by workup as described above yielded 0.4 g (2.4 mmol) of 1,2-di-4-pyridyl-1,2-diphenylethane (20% overall yield, 30% current yield). Physical and spectroscopic data are as follows: mp 326–330 °C dec (lit.[15] mp 242–245 °C; ^{1}H NMR (CD_3COOD) δ 5.8 (2 H, s), 7.2–7.5 (12 H, m), 7.6 (2 H, d), 8.3 (2 H, d), 8.7 (2 H, d); ^{13}C NMR (CD_3COOD) δ 55.2, 127.8, 129.2, 129.5, 130.6, 139.2, 142.8, 163.9; mass spectrum, *m/e* (relative intensity) 336 (37), 169 (22), 168 (100), 167 (43), 115 (11). This agrees well with the previously reported spectrum.[15] Diastereselectivity was determined by integration of the signals at 5.78 and 5.82 ppm.

Homogeneous Oxidative Dimerization of Benzylpyridine Anions. The procedure of Skattebol[15] was modified. To a solution of 3.5 mL of diisopropylamine (2.5 g, 25.0 mmol) in 25 mL of ether was added 16 mL of 1.6 M methyllithium (25.6 mmol). After 5 min, 4.0 mL (4.0 g, 24 mmol) of the benzylpyridine was added by syringe. The resulting dark red solution was added dropwise to a stirred solution of 2.5 mL of methanesulfonyl chloride (3.7 g, 32 mmol) in 15 mL of ether. During addition the precipitation of lithium chloride made stirring difficult. After addition, water was added and the product was isolated by filtration. Recrystallization from ethanol–benzene gave pure samples. The diastereoselectivities were determined as previously described and Table V records the yields and diastereselectivities for each benzylpyridine anion.

Preparation of Pyridyldiphenylmethane Anions for NMR Studies. An oven-dried 5-mm NMR tube was charged with 0.2 mL of deuteriated benzene under argon. The anion solution (0.5 M in THF with 2% Me_4Si) was added by syringe and the NMR tube was capped and sealed. For the p*K* studies, the solution also contained a known quantity of another known reference acid as described for a typical experiment below.

A solution of 0.4 M lithio-2-pyridyldiphenylmethane in THF and an equimolar amount of 4-benzylpyridine (p*K* = 25.2 ± 0.2)[3] were placed in an NMR tube and the proton NMR was recorded (see paragraph at the end of paper about supplementary material). A singlet at 3.8 ppm (2 H) is unique for 4-benzylpyridine and the singlet at 4.7 (1 H) is unique for lithio-4-benzylpyridine. Similarly 2-pyridyldiphenylmethane has a nonoverlapped peak at 5.6 ppm (1 H) and lithio-2-pyridyldiphenylmethane has a nonoverlapped triplet at 5.5 ppm (1 H).

In the competition experiment all species except the anion of 2-pyridyldiphenylmethane are present in significant quantities. From the known detection limits the p*K* of 2-pyridyldiphenylmethane is estimated to be greater than 26 p*K* units. The spectra for the competition experiment was identical when the initial solution was lithio-4-benzylpyridine and 2-pyridyldiphenylmethane. All equilibration experiments were approached from both sides.

When 2-benzylpyridine (p*K* = 28.3 ± 0.2)[8] was used in place of 4-benzylpyridine, all four species were present at equilibrium. Integration of the peak areas leads to a value for the p*K* of 2-pyridyldiphenylmethane of 27.5 ± 0.3 p*K* units.

For 3-pyridyldiphenylmethane, the reference acids were 2-benzylpyridine and 2-pyridyldiphenylmethane. For 4-pyridyl-

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(19) Olah, G. A. *Synthesis* 1978, 397.

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diphenylmethane the reference acids were fluorene (pK = 24.4 ± 0.2)[3] and 4-benzylpyridine (pK = 25.3 ± 0.2).[8] The pK values for these and other acids are recorded in Table IV.

Acknowledgment. We are grateful to Prof. R. Reed for generously providing the electrosynthetic cell and valuable information.

Registry No. (Diphenylmethyl)lithium, 881-42-5; [(pyridin-3-yl)phenylmethyl]lithium, 97254-18-7; [(pyridin-2-yl)phenylmethyl]lithium, 56501-99-6; [(pyridin-4-yl)phenylmethyl]lithium, 81771-00-8; (triphenylmethyl)lithium, 733-90-4; [(pyridin-3-yl)diphenylmethyl]lithium, 109283-60-5; [(pyridin-2-yl)diphenylmethyl]lithium, 83425-78-9; [(pyridin-4-yl)diphenylmethyl]lithium, 83425-79-0; anthracene, 120-12-7; 1,1,2,2-tetraphenylethane, 632-50-8; 1,2-di-2-pyridyl-1,2-diphenylethane, 28830-48-0; 1,2-di-3-pyridyl-1,2-diphenylethane, 109283-61-6; 1,2-di-4-pyridyl-1,2-diphenylethane, 24559-23-7; 2-pyridyldiphenylmethane, 3678-70-4; 3-pyridyldiphenylmethane, 3678-71-5; 4-pyridyldiphenylmethane, 3678-72-6.

Supplementary Material Available: CV and DPV for lithio-4-benzylpyridine and anthracene in THF solution and NMR competition spectra (2 pages). Ordering information is given on any current masthead page.

Stereospecific Anti Radical Elimination Reaction from β-Nitro Sulfones

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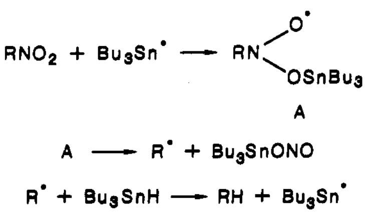
β-Nitro sulfones react with tin radicals to give alkenes, where the nitro and sulfonyl groups are cleaved in an anti stereospecific way. This specificity is lost when the elimination reaction is induced by sodium sulfide. The high stereospecificity of the reaction induced by tin radicals can be interpreted by assuming that the organotin group is close to the nitro group to form a nitroxide radical, which undergoes the stereospecific cleavage of the nitro and sulfonyl groups via successive β-scission of radicals.

Recently, Tanner's group and ours reported a novel reductive cleavage of the carbon–nitrogen bond of aliphatic nitro compounds.[1] It has been proposed that alkyl radicals are formed from anion radical intermediates of nitro compounds, which are formed via a one-electron-transfer process from tin radicals to nitro compounds.[1] Giese also reported that anion radicals are detected by ESR measurements during denitration of nitro sugars with tin radicals,[2] where a tight radical ion pair is proposed as an intermediate.[2] Such anion radicals can be regarded as nitroxide radicals,[3] and the difference between these two species should be very small. Thus, denitration with tributyltin hydride is now believed to proceed via the mechanism shown in Scheme I.

Scheme I



Formation of alkyl radicals from the anion radicals of nitro compounds has been well established in $S_{RN}1$ reactions of nitro compounds.[4] The mechanism of Scheme I is the same as that of $S_{RN}1$ except that a loose radical ion pair is generally involved as an intermediate in $S_{RN}1$. The intermediate A, which is formed by the reaction of tin radicals with nitro compounds, shows a slightly different reactivity from the anion radicals, which are formed by the reaction of nitro compounds with stabilized carbanions or sodium thiophenoxide. For example, the anion radicals formed by the reaction of α-nitro sulfones with stabilized carbanion, sodium thiophenoxide, or 1-benzyl-1,4-dihydronicotinamide (BNAH) undergo the smooth elimination reaction of the sulfinate ion to give α-nitroalkyl radicals.[5,6] On the other hand, tin radicals are inert to α-nitro sulfones under the usual denitration conditions using tributyltin hydride.[7] Thus, the intermediate A, which is generated by the reaction of tin radicals with nitro compounds, is slightly different from the intermediate of an $S_{RN}1$ reaction of nitro compounds, which is formed in dipolar aprotic solvents with sodium or potassium as a countercation. In order to get more precise information on the reductive cleavage of aliphatic nitro compounds with tin radicals, study of the stereochemistry of the reductive elimination reaction of nitro compounds has been undertaken. Aliphatic nitro compounds such as compounds **1** having radical leaving groups at the β-position undergo reductive cleavage in the radical elimination reaction to give alkenes **2**[8] (eq 1). Thus, *vic*-dinitro compounds, β-nitro sulfones, and β-nitro sulfides are converted into alkenes **2** on treatment with Na_2S,[9] Ca/Hg,[10] Bu_3SnH,[11] or NaTeH.[12]

We have found that the elimination reaction of β-nitro sulfones with tin radicals proceeds with high stereospec-

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