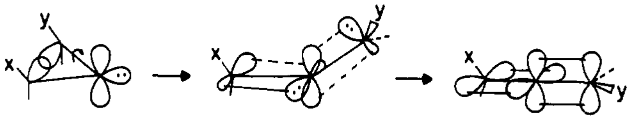
group can promote or retard—by electronic effects—the rotation of one group relative to the other during the ring-opening process. In other words, in Scheme I, paths "a" and "b" cannot be occurring to exactly the same extent.

Preference for one path over the other (Chart I) can be rationalized as follows. Applying a correlation diagram based approach to the problem of this type of interconversion, Borden[11,12] has concluded that singlet cyclopropylidene opens by preferentially rotating only one terminal carbon. Assuming the carbene is sp^2 hybridized, then the carbon that rotates becomes the one that furnishes the pair of electrons to the carbene center. This process would certainly be expected to be sensitive to electronic effects. The question of which type of group (electron withdrawing or electron donating) promotes rotation must remain open until anticipated absolute configuration studies are completed.



Acknowledgment. The authors are grateful to the National Science Foundation for support of this work.

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[11] Private communication from W. T. Borden of Harvard University. Some of Professor Borden's results have also been discussed in H. R. Ward and E. Karafiath, *J. Amer. Chem. Soc.*, **91**, 7474 (1969). See also W. T. Borden, *Tetrahedron Lett.*, 447 (1967), for a discussion of ring opening of the triplet. We are deeply indebted to Professor Borden for communicating his results to us.

[12] The ring opening has also been treated theoretically by M. J. S. Dewar, E. Haselbach, and M. Shanshal, *J. Amer. Chem. Soc.*, **92**, 3505 (1970).

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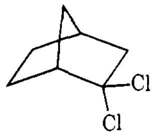
Anomalous Proton Donor Effects in Dimethylformamide

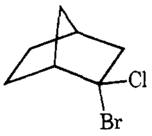
Sir:

Phenols and carboxylic acids, although largely undissociated in dimethylformamide (DMF), are nevertheless good proton donors in this solvent toward electrochemically generated radical anions of aromatic hydrocarbons and carbonyl compounds.[1] By contrast, water is known to be a rather poor proton donor toward aromatic radical anions in DMF.[2,3] Mark has suggested that the low proton-donating ability of water in DMF is due to the high degree of structure in water–DMF solutions, demonstrated, *e.g.*, by such data as the large amounts of heat evolved upon mixing water and DMF, and the substantially increased viscosity of the resulting solutions relative to the viscosities of the individual components. On the other hand, water and acetonitrile are not strongly associated, and indeed water is a much better proton donor in this solvent.[3] Likewise, methanol and DMF are not strongly associated, and methanol is a much better proton donor than water in DMF.[3] We wish to report discovery of a system in which the proton-donating ability of phenols and acetic acid is extremely low relative to water, methanol, or even tetraethylammonium ion.

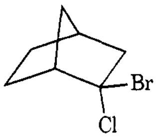
Electrochemical reduction of dihalides **1–3**[4] in DMF containing tetraethylammonium bromide (TEAB)[5] affords in each case the same mixture of nortricyclene (**4**) (62%) and *endo*-norbornyl chloride (**5**) (38%).[6] We interpret isolation of the same products in the same ratio from all three dihalides as convincing evidence for generation of the same intermediate, equilibrating anion **6**, from all three (Scheme I). Ejection of chloride ion from **6** would lead to carbene **7**, which is known to undergo efficient intramolecular insertion to form **4**.[7] Alternatively, protonation of **6** from the less hindered exo side[8] would afford **5**. Evidence that TEAB is a proton donor in the latter path is the formation of ethylene, demonstrated by vpc analysis. This process has been observed by others during electrochemical reduction of alkyl halides.[9] A corollary of the mechanism suggested in Scheme I is that addition of a proton donor to the medium should increase the ratio of **5** to **4** by capturing **6** before it can eject chloride ion. We have found that added methanol or water does indeed increase the ratio of **5** to **4**. This ratio, as expected, is dependent upon the concentration of added proton donor; the ratio of **5** to **4** is increased from the original 38:62 to 80:20 when the water con-



1

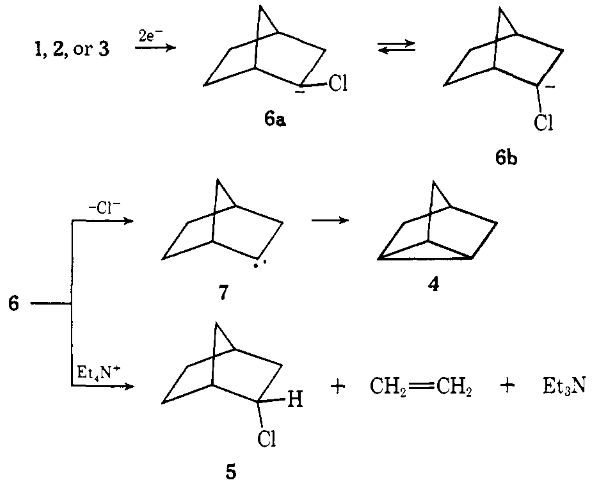


2



3

Scheme I



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[1] For a recent review, see M. J. Peover, *Electroanal. Chem.*, **2**, 1 (1967).

[2] D. L. Maricle, *Anal. Chem.*, **35**, 683 (1963).

[3] J. R. Jezorek and H. B. Mark, Jr., *J. Phys. Chem.*, **74**, 1627 (1970).

[4] A. J. Fry, W. B. Farnham, B. J. Holstein, M. A. Mitnick, and L. C. Riggs, *J. Org. Chem.*, **34**, 4195 (1969).

[5] Dimethylformamide was purified by reflux over 4A molecular sieve, followed by distillation *in vacuo* from molecular sieve; water content, determined by vpc analysis (5 ft × 1/4 in., Porapak Q, 210°), is typically 2–4 m*M*. DMF is very hygroscopic; the actual water content of the electrolysis mixtures is 15–20 m*M*. TEAB was recrystallized from ethanol–ether and dried overnight in a vacuum desiccator.

[6] 2% of *exo*-norbornyl chloride could easily have been detected under our vpc conditions (50 ft × 1/8 in. column, packed with 7% Zonyl E-7 on Chromosorb G, 75°, flow rate 25 ml/min).

[7] W. G. Dauben and F. G. Willey, *J. Amer. Chem. Soc.*, **84**, 1497 (1962).

[8] *E.g.*, (a) H. C. Brown and K.-T. Liu, *ibid.*, **92**, 200 (1970); (b) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970).

[9] J. L. Webb, C. K. Mann, and H. M. Walborsky, *ibid.*, **92**, 2042 (1970).

centration is 1 M. Ethylene formation is also suppressed at high water concentrations. Remarkably, however, *added acetic acid or phenols*[10] *(1 M) have little effect upon this ratio.*[11] Furthermore, ethylene formation from the Hoffman elimination upon the supporting electrolyte (0.1 M) is not quenched by added phenols. Thus in this system tetraethylammonium ion is a more efficient proton donor toward anionic intermediates in the reduction of **1**, **2**, or **3** than are phenols, even when the latter are in tenfold excess! These results clearly imply that phenols and acetic acid are not incorporated into the inner layer[12,13] at the interface between the mercury electrode and the solution, since it is in this region that the carbanion is formed and is reacting. Added water or methanol can, however, be incorporated into this region. The surface concentration of water is lower than its concentration in bulk solution (or in the diffuse[12] part of the double layer). This is demonstrated both by electrocapillary data[14] and by our observation that generation of **6** by reaction between **1** and electrochemically generated naphthalenide ion in DMF containing 50 mM water affords a 60:40 mixture of **5** and **4**, while this ratio is 48:52 in the direct electrolysis of **1** in DMF containing 50 mM water. The decreased surface concentration of water relative to bulk solution is no doubt due in part to preferential adsorption of both tetraethylammonium ion (R_4N^+) and DMF, this adsorption having the effect of "squeezing out" water from the inner layer.[12,14] We have tested this hypothesis by changing the electrolyte to triethylammonium bromide ($R_3NH^+Br^-$). We expected by this artifice to incorporate a much stronger acid into the double layer. This expectation was confirmed: the ratio of **5** to **4** was changed from 38:62 to 92:8 with the change in electrolyte. The synthetic implications of this experiment are obvious.

Much more work will be necessary before these effects are understood. The significance for electrochemical investigations is clear, however; it is often supposed that phenol and carboxylic acids are efficient proton donors toward anions in DMF, and conversely, that failure to quench an electrochemical reaction by addition of one of these implies that it does not involve carbanionic intermediates. While these conclusions may often be justified, our results imply that neither need necessarily be true.[15]

Acknowledgment. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation. The Electrochemical Society awarded a Colin Garfield Fink summer fellowship to R. G. R. Experimental conditions for the water analysis by vpc were worked out by Mr. Richard C. Reed and Mr. Walter Morgan. Professor Harry B. Mark made a number of valuable comments upon the manuscript.

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(10) Phenol, hydroquinone, and 2,4,5-trimethylphenol were all tried.

(11) A slight decrease in the relative proportion of **4** is observed in the presence of 1 M phenols, if $[H_2O] < 100$ mM, but this effect is much less than that produced by addition of 1 M water. Similar results are observed for acetic acid where $[H_2O] < 350$ mM.

(12) D. M. Mohilner, *Electroanal. Chem.*, **1**, 241 (1966).

(13) Electrocapillary curves show that phenol and resorcinol are not specifically adsorbed on the mercury surface in DMF: J. Janata, J. Gendell, R. G. Lawton, and H. B. Mark, Jr., *J. Amer. Chem. Soc.*, **90**, 5226 (1968), footnote 15.

(14) R. Payne, *Advan. Electrochem. Electrochem. Eng.*, **7**, 1 (1970).

(15) Dihalides **1**–**3** have polarographic half-wave potentials of −1.54, −0.93, and −0.83 V, respectively, relative to the reference electrode of Marple.[16] Preparative electrolyses were carried out at controlled potential, at *ca.* −1.8 V for **1** and −1.1 V for **2** and **3**. These potentials are considerably cathodic of the electrocapillary maximum, which is at *ca.* 0 V in this system, as determined by electrocapillary measurements.

(16) L. W. Marple, *Anal. Chem.*, **39**, 844 (1967). This electrode is *ca.* −0.7 V relative to sce.

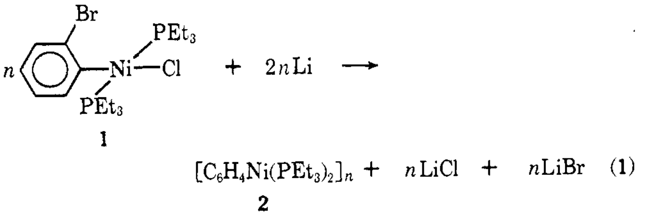
Synthesis of a Nickel Heterocycle

Sir:

We wish to report a new type of transformation in organo–transition metal chemistry. Treatment of diethyl ether solutions of *trans*-chloro(2-bromophenyl)-bis(triethylphosphine)nickel(II)[1] (**1**) with lithium metal at −40 to −78° has afforded essentially quantitative yields of lithium bromide, lithium chloride, and of an organonickel compound, **2**, derived from removal of the halogen elements from **1**. Compound **2** is a bright yellow crystalline solid at room temperature and is extremely air sensitive. All experiments were therefore conducted with the rigorous exclusion of atmospheric oxygen and moisture by using standard vacuum-line techniques. The compound slowly decomposes at room temperature, but it can be stored for months *in vacuo* at −78° and its solutions are stable for hours at 0°.

The progress of the reaction of **1** with lithium was monitored by following the change in the aromatic pmr spectrum with time. The unsymmetrical spectrum of **1** was gradually converted to a symmetrical AA′BB′ spectrum, and no pmr evidence for an intermediate species was obtained. The chemical change only occurred when lithium metal was present.

The stoichiometry, as indicated by eq 1, was demonstrated in the following manner. Compound **1** was treated with an accurately measured moderate excess of



1

$$[C_6H_4Ni(PEt_3)_2]_n + n\,LiCl + n\,LiBr \qquad (1)$$

2

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(1) Treatment of *trans*-dibromobis(triethylphosphine)nickel(II) with 2-bromophenylmagnesium bromide in diethyl ether[2] or oxidative addition of *o*-dibromobenzene to ethylenebis(triethylphosphine)nickel-(0) afforded **1**, mp 105.1–105.3°, after chromatography of the product on Baker aluminum oxide Analytical Reagent for Chromatography, pH 3.8. Bromide bonded to nickel in the primary product was quantitatively replaced by chloride on the alumina column. The general experimental procedure used in the oxidative-addition reaction was essentially the same as that described for the synthesis of *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II),[3] with the exception that a longer reaction time was employed. This procedure afforded a 52% yield of **1**. The extension of this method to the preparation of arylnickel compounds was first demonstrated by Fahey.[4]

Satisfactory analyses were obtained for **1** and for iodo compound **3** which is described in the text.

(2) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

(3) (a) R. G. Miller, D. R. Fahey, and D. P. Kuhlman, *J. Amer. Chem. Soc.*, **90**, 6248 (1968); (b) R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, *ibid.*, **92**, 1511 (1970).

(4) D. R. Fahey, *ibid.*, **92**, 402 (1970).