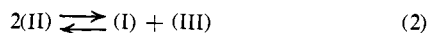


Figure 1. Cyclic voltammogram of differrocenylacetylene in CH_2Cl_2 containing $n\text{-Bu}_4\text{NBF}_4$ (0.2 M), sweep rate 200 mV/sec.

in methylene chloride is shown in Figure 1. In the anodic scan, two separate peaks are observed at 640 and 775 mV. Reduction peaks in the corresponding cathodic scan are found at 580 and 710 mV. The voltammogram is characteristic of a compound undergoing two reversible one-electron oxidations at close potentials, a feature which has been shown to be characteristic of weakly interacting bridged biferrocenes.^{3,4}

Analysis of the voltammetric data (differences in peak potentials taken as representative of differences in redox potentials) indicates that a solution of II will disproportionate, as in eq 2. Approximately 90% of the



species in the equilibrium mixture at 25° are the mixed-valence monocations. This will probably preclude isolation of II, but the spectroscopic features can still be analyzed when the above ratios are taken into account.

To obtain absorption spectra of the cations of differrocenylacetylene, 10^{-3} M solutions were generated electrochemically. Oxidation by precisely 1 F/mol yields a deep violet solution which was analyzed by polarography. Although separate waves are not obtained, the $I_{\text{ox}}/I_{\text{red}}$ ratio was shown to be unity, indicating a current yield of 100%. Exhaustive coulometric oxidation resulted in the consumption of precisely 2 F/mol. Cyclic voltammetry and polarography clearly demonstrated the stability and identity of the resulting pale green dication (III). (Solutions are stable when protected from air and moisture.)

The visible-near-infrared spectra of differrocenylacetylene and its mono- and dications are shown in Figure 2. Absorptions in the visible at 545 nm (ϵ 2100) for the monocation and 720 nm (ϵ 1000)⁵ for the dication are typical of ferrocenium ions and are assigned to the ${}^2E_{2g} \rightarrow {}^2A_{1g}$ transition.⁶ These bands are considerably shifted with respect to the unsubstituted ferrocenium ion (λ_{max} 617 nm, ϵ 420).⁶

(3) J. E. Gorton, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, **27**, 4353 (1971).

(4) W. H. Morrison, Jr., S. Krogsrud, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 1998 (1973).

(5) The maximum at 545 nm in the spectrum of the dication is probably due to a small amount of monocationic impurity.

(6) R. Prins, *Chem. Commun.*, 280 (1970).

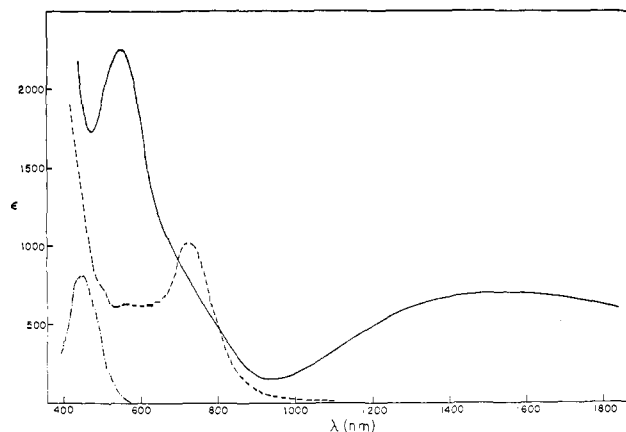
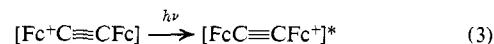


Figure 2. Visible and near-infrared spectra of differrocenylacetylene (---), the differrocenylacetylene monocation (—), and the differrocenylacetylene dication (- · -) in CH_2Cl_2 containing 0.1 M $n\text{-Bu}_4\text{NBF}_4$.

In addition, there is a broad band in the near-infrared spectrum of the mixed-valence monocation centered at 1560 nm (ϵ 670). This band is absent in both the neutral (I) and fully oxidized (III) species and is assigned to an intervalence transfer transition (eq 3).^{1,7}



Intervalence transfer transitions in the near-infrared had previously been observed only in biferrocene-type molecules in which the ferrocene and ferrocenium portions are directly fused.^{1,8,9} No corresponding low energy transitions have been observed for biferrocenes bridged by saturated groups.⁹⁻¹¹ The observation of a mixed-valence transition in the differrocenylacetylene monocation indicates that the intervalence electron transfer can occur exclusively through the ligand system, inasmuch as the iron-iron distance (estimated to be 6.5 Å in a cis conformation and 7.3 Å in a trans) is too large to involve direct metal-metal overlap.

Acknowledgments. The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Advanced Research Projects Agency for grant support of this research.

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(11) W. H. Morrison, Jr., and D. N. Hendrickson, *Chem. Phys. Lett.*, **22**, 119 (1973).

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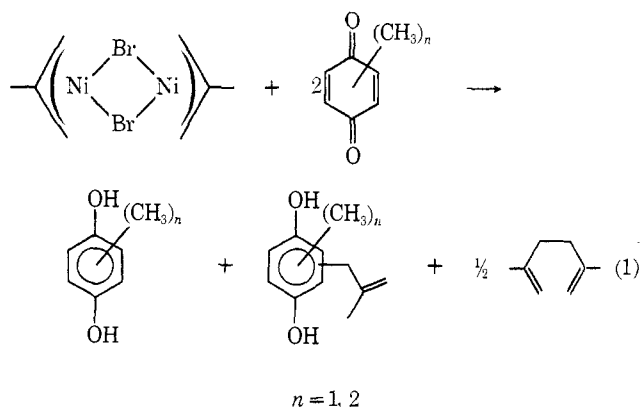
Received June 24, 1974

Reactions of π -2-Methylallylnickel Bromide with Methylbenzoquinones. Evidence for Electron Transfer

Sir:

We recently reported the reaction between π -allylnickel bromide complexes and quinones to produce allylhydroquinones and speculated that it proceeded

by a 1,4-addition mechanism.¹ Further study of this reaction with a series of methyl- and dimethylbenzoquinones has revealed several features which strongly suggest that electron transfer processes are involved. When the reaction is run under conditions for maximum yield² all products are obtained in the *reduced* state as hydroquinones. The reaction has the stoichiometry expressed in eq 1, wherein 1 equiv of quinone is reduced



and alkylated, 1 equiv is simply reduced, and 1 equiv of the available allyl groups is obtained as biallyl. This 1:1 ratio of reduced to reduced-and-alkylated quinone is observed regardless of the initial ratio of reactants.

The reactivity of the various quinones studied parallels their reduction potentials, the more easily reduced quinones being the most reactive. Specifically, quinones which will accept an electron at potentials less negative than -0.7 V vs. sce will react with π -allyl-nickel bromides while quinones with reduction potentials more negative than -0.7 V are recovered unchanged. Thus, benzoquinone ($E_{1/2} = -0.58$ V), methylbenzoquinone ($E_{1/2} = -0.62$ V), and dimethylbenzoquinones ($E_{1/2} = -0.70$ V) react while trimethylbenzoquinone ($E_{1/2} = -0.80$ V) and tetramethylbenzoquinone ($E_{1/2} = -0.88$ V) are unreactive.³ This correlation closely resembles that observed in the reaction of lithium dimethylcuprate with conjugated enones, a system for which a compelling case for electron transfer has been made.⁴ That electron transfer (reduction) occurs *prior* to allyl group transfer is suggested by the observation that quenching of the reaction mixture with aqueous HCl prior to warming to room temperature leads predominately to reduction of the quinone to the hydroquinone, with virtually no alkylation product being obtained.

Finally, the *site* of alkylation of the various methylbenzoquinones studied corresponds to the *noncarbonyl*

(1) L. S. Hegedus, E. L. Waterman, and J. Catlin, *J. Amer. Chem. Soc.*, **94**, 7155 (1972).

(2) All reactions were run under an argon atmosphere. The nickel complex (1 mmol) in 10 ml of DMF was added dropwise to the quinone (2 mmol) in 20 ml of DMF at -50° . The resulting deep blue-green solution was stirred at -50° for 2 hr, warmed to 25° over 2 hrs, and stirred at 25° for an additional 2-4 hr. The resulting clear brown-green solution was partitioned between ether and 1.2 N HCl, and the ether phase dried over anhydrous magnesium sulfate. After removal of solvent, the crude material was purified by preparative tlc (Si gel, elution with 2:1 pentane-ether).

(3) The $E_{1/2}$ values for the quinones discussed in this study and in the initial paper (ref 1) were measured in DMF with 0.1 M *n*-Bu₄NBF₄ as supporting electrolyte and are reported relative to sce.

(4) H. O. House and M. J. Umen, *J. Amer. Chem. Soc.*, **94**, 5495 (1972).

quinone radical anion, as measured from esr hyperfine splitting constants and as calculated by Huckel LCAO-MO methods.⁵⁻⁷ Table I shows this correlation by

Table I. Spin Densities of Quinone Radical Anions and Products from Eq 1^a

| | | |
|--|--|---------------------------------|
| | 38% (15) 50% (20) 12% (5) trace | + methylhydroquinone (44) |
| | 100% (48) | + 2,3-dimethylhydroquinone (50) |
| | 100% (47) | + 2,5-dimethylhydroquinone (42) |
| | 100% (46) | + 2,5-dimethylhydroquinone (47) |

^a The per cent figures refer to the amount of a particular allyl product relative to the total amount of allyl product obtained. The numbers in parentheses refer to the *isolated* yield of each product based on the starting quinone as limiting reagent.

ring site of highest spin density in the corresponding listing the calculated spin densities for the various quinone radical anions followed by the allyl products obtained from the reactions summarized in eq 1.⁸ With the minor exception of the small amount of 2-attack with methylbenzoquinone, there is a striking correlation. It is clear that the free quinone radical anion is not the reactive intermediate since the site of highest spin density in this species is the carbonyl group, which does not undergo attack in these reactions.⁹ Instead, it is likely that the electron transfer step is followed by immediate coordination of the reduced quinone species to the nickel complex, and alkyl transfer occurs in this complexed intermediate, in a fashion similar to that proposed in the alkylation of conjugated enones by lithium dimethylcuprate.⁴ The exact nature of the reactive intermediates and a more detailed description

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(6) M. Hriska, *Collect. Czech. Chem. Commun.*, **34**, 1665 (1969).

(7) A. Farbourn and E. A. C. Lucken, *J. Chem. Soc.*, 258 (1963).

(8) All products in Table I were isolated and purified. All products had infrared, nmr, and mass spectra consistent with the proposed structures, and all had acceptable elemental analyses. The mixture of isomers from the reaction with methylbenzoquinone was unseparable. The mixture was oxidized to the corresponding quinones. A 100-MHz nmr spectrum nicely resolved the aromatic region into three absorptions due to the three different isomers: δ 6.75 (s, 12%, 2,3-disubstituted), 6.61 (q, 38%, 2,5-disubstituted), 6.56 (m, 50%, 2,6-disubstituted). Assignments were made by comparison with the corresponding dimethylquinones. The eno-dione products had characteristic infrared and nmr spectra that easily distinguished them from quinoid products.

(9) When benzoquinone is reduced electrochemically in DMF to its radical anion in the presence of 2-methylallyl bromide, the monomethylallyl ether of hydroquinone is the sole product.

of the mechanism of this unusual reaction are under current investigation.

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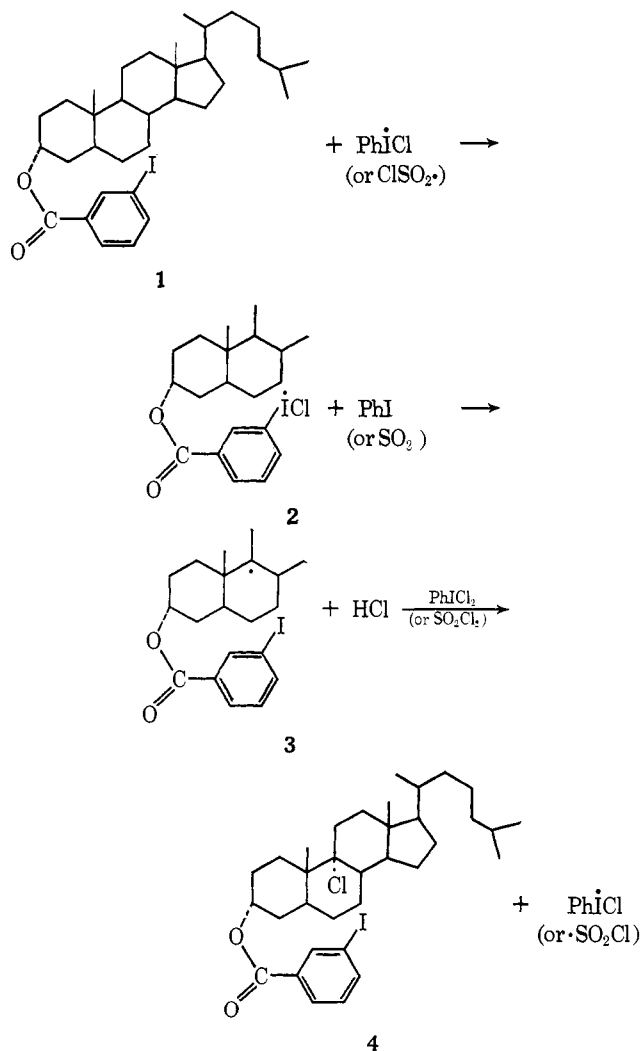
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Remote Functionalization of Steroids by a Radical Relay Mechanism

Sir:

We have described the use of phenyliodine dichloride in steroid functionalizations¹ and the conversion of this intermolecular halogenation process into a directed intramolecular reaction.² For example, 3 β -cholestanol was converted with *m*-iodobenzoic acid and triphenylphosphine-diethyl azodicarboxylate into the *m*-iodobenzoate of 3 α -cholestanol (**1**) in 85% yield by the very useful inversion-esterification procedure.³ This was converted with Cl₂ to the attached ArICl₂ derivative, and on brief irradiation this afforded the *m*-iodoben-



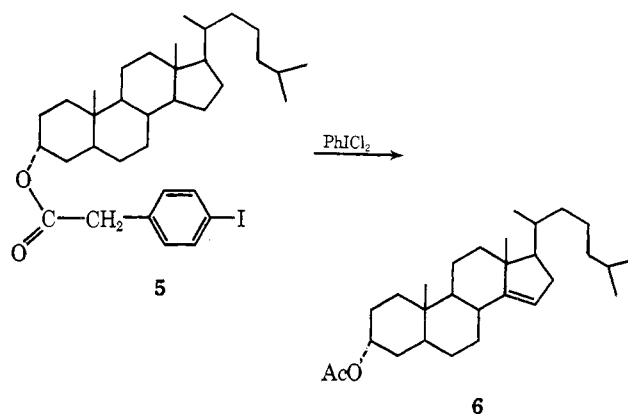
(1) R. Breslow, J. A. Dale, P. Kalicky, S. Y. Liu, and W. N. Washburn, *J. Amer. Chem. Soc.*, **94**, 3276 (1972).

(2) R. Breslow, R. Corcoran, J. A. Dale, S. Y. Liu, and P. Kalicky *J. Amer. Chem. Soc.*, **96**, 1973 (1974).

(3) A. K. Bose, B. Lal, W. A. Hoffman, and M. S. Manhas, *Tetrahedron Lett.*, 1619 (1973).

zoate of 9 α -chloro-3 α -cholestanol (**4**) as the major product.² The important intermediate in the hydrogen abstraction from the steroid is species **2**, which can be considered to be a σ -complex of Cl• with the attached aryl iodide. We now wish to report that **2** can instead be generated by transfer of a chlorine atom to **1** from an external radical reagent species. The overall process **1** \rightarrow **2** \rightarrow **3** \rightarrow **4** has a number of advantages over the direct use of an aryl dichloride prepared from an attached aryl iodide such as **1**. Thus an excess of the chlorinating agent can be used, and exposure of sensitive substrates to Cl₂ is avoided. These advantages made possible the cortisone acetate synthesis described in the accompanying communication.⁴

A solution of **1** (742 mg, 1.20 mmol) and PhICl₂ (330 mg, 1.20 mmol) in 120 ml of CH₂Cl₂ was irradiated with a 275-W sunlamp for 25 min at 25° under N₂. Saponification, acetylation, and chromatography afforded 18.4% of unfunctionalized 3 α -cholestanol acetate and 66% $\Delta^{9(11)}$ -cholestene-3 α -ol acetate (80% yield corrected for recovered starting material) with 12% of polar impurities and no detectable amount of a Δ^{14} -cholestanol derivative. By contrast, the same reaction conditions applied to the *p*-iodophenyl acetate of 3 α -cholestanol (**5**) led to 55% recovery of unfunctionalized steroid and 18% production of Δ^{14} -cholestanol acetate with 27% of polar impurities and no detectable amount of $\Delta^{9(11)}$ -steroid derivative. The preference of **1** to undergo chlorination of C-9 while **5** is



chlorinated at C-14 are those expected from molecular models if hydrogen is being abstracted by a chlorine atom attached to iodine, and they are the same preferences we have previously observed² starting with the aryl iodine dichlorides derived from **1** and **5**. Thus, the most trivial explanations of these observations would be conversion of **1** to the corresponding dichloride by reaction with PhICl₂, but this is excluded by direct equilibration studies. The characteristic aryl proton nmr of **1** dichloride cannot be observed after 18 hr equilibration of **1** with PhICl₂ in the dark at 0.05 *M* in CH₂Cl₂ solution nor can equilibration be detected (within 10%) starting with **1** dichloride and PhI after the same time. Aliquots withdrawn during the irradiation of **1** with PhICl₂ also reveal no detectable amount of **1** dichloride.

Further observations support the mechanism shown. It should be possible to transfer Cl• to **1** from other species, and we find that this can be done using sulfonyl chloride. Thus a 0.01 *M* solution of **1** in CCl₄ with

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