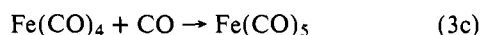
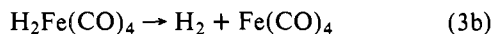
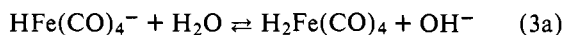
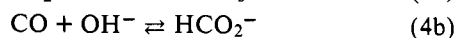
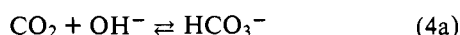


ever, below  $\sim 140$  atm the conversion became quite rapid with the formation of  $\text{HFe}(\text{CO})_4^-$  being complete within minutes. These observations imply that step 2a can be written as an equilibrium when anhydrous nonhydroxylic solvents are used.

An alternative mechanism for the iron carbonyl catalyzed water gas shift reaction involves the participation of  $\text{H}_2\text{Fe}(\text{CO})_4$ . The key steps for hydrogen evolution are shown in Eq 3a-c (which are possible substitutes for 2a + 2b in the mechanism given above):



A detailed study of the effects of CO pressure and base concentration on the rates of  $\text{H}_2$  and  $\text{CO}_2$  evolution for the iron carbonyl catalyzed reaction should allow identification of the operative mechanism, but the existence of the equilibria 4a and 4b complicate interpretation to the degree that the data at hand are insufficient for a definitive mechanistic assignment.



Similarly, with the  $\text{Mo}(\text{CO})_6/\text{KBH}_4$  system the possibility exists that  $\text{HMO}_2(\text{CO})_{10}^-$  may be an intermediate in the reaction scheme. The anions  $\text{HM}_2(\text{CO})_{10}^-$  have been shown<sup>15</sup> to form in reactions of  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo},$  and  $\text{W}$ ) with  $\text{BH}_4^-$  in donor solvents at elevated temperatures.

Despite the mechanistic ambiguities still remaining, our work clearly indicates that the range of metal carbonyls which can be used as catalyst precursors for the water gas shift reaction is far greater than that suggested by previous results.<sup>1,2</sup> In particular, carbonyls of relatively inexpensive metals such as chromium, molybdenum, tungsten, and iron as well as those of rare and expensive metals such as ruthenium<sup>1</sup> and rhodium<sup>2</sup> can give catalytically active systems for this important reaction.

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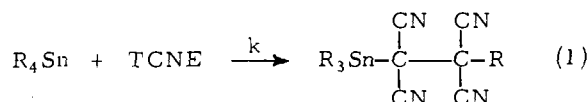
Received August 19, 1977

## Photoassisted Intermolecular Charge-Transfer Processes for Organometals: Insertion of Tetracyanoethylene and Spin Adducts with Quinones

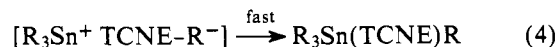
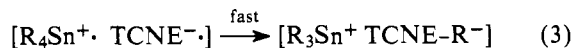
Sir:

Organometals can react readily with a variety of compounds under mild conditions to produce paramagnetic intermediates as a result of charge-transfer interactions in which the organometal functions as the donor. We wish to show that the same process can be introduced photochemically by irradiation of the charge-transfer band at low temperatures, or with organometals in which the thermal reactions do not occur.

The addition of TCNE to various tetraalkyllead and -tin compounds results in a transient charge-transfer spectrum, the disappearance of which coincides with the formation of 1,2 adducts (eq 1), which have been well characterized.<sup>1</sup> From the

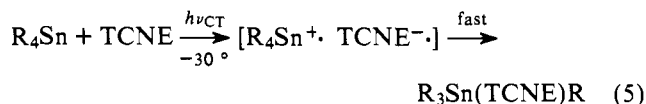


structural effects on kinetics and selectivities it was shown that the thermal addition occurred by the following mechanism:



The rate-limiting step in eq 2 is an electron-transfer process which accords with the linear relationship observed between  $\log k$  and  $\lambda_{\text{max}}$  of the charge-transfer band as well as the ionization potentials of the organometals.<sup>1</sup> Thus, for the family of group 4b alkyl metals, the rates of insertion decrease precipitously in the order:  $\text{PbEt}_4 \gg \text{SnEt}_4 \gg \text{GeEt}_4 > \text{SiEt}_4$ , as a result of the rising trend in their ionization potentials from 8.13, 9.01, 9.40 to 9.78 eV, respectively.

If this mechanism is correct, the direct irradiation of the charge-transfer band should also promote the same insertion reaction in eq 1 except at lower temperatures. Indeed, we now find that the process in eq 1 can be carried out photochemically by the irradiation at the charge-transfer band under conditions in which the thermal reaction is too slow. For example, the charge-transfer band of the  $\text{Et}_4\text{Sn}$ -tetracyanoethylene (TCNE) complex occurs at 426 nm, and the half-life for disappearance is  $\sim 6$  h at 30 °C. At -30 °C the charge-transfer complex is stable and no addition occurs within 2 h. However, irradiation with a 100-W medium-pressure Hg lamp at 426 nm (using a Jarrell-Ash 82-410 monochromator) affords a 50% yield of the same adduct within this period:



Similar results have been obtained with  $\text{Me}_4\text{Sn}$ , in which the addition to TCNE in eq 1 proceeds with second-order kinetics when carried out thermally. The temperature dependence of the second-order rate constant  $k$  shows an activation energy of  $\Delta H^\ddagger = 13$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -41$  eu, for this addition. In marked contrast, the rate of the photochemically induced addition is unchanged between -30 to +20 °C, when the concentration of the reactants and the light intensity are held constant. The related compounds  $\text{Et}_4\text{Ge}$  and  $\text{Et}_4\text{Si}$  do not undergo significant insertion of TCNE thermally at 30 °C. However, TCNE adducts similar to those in eq 1 can be ob-

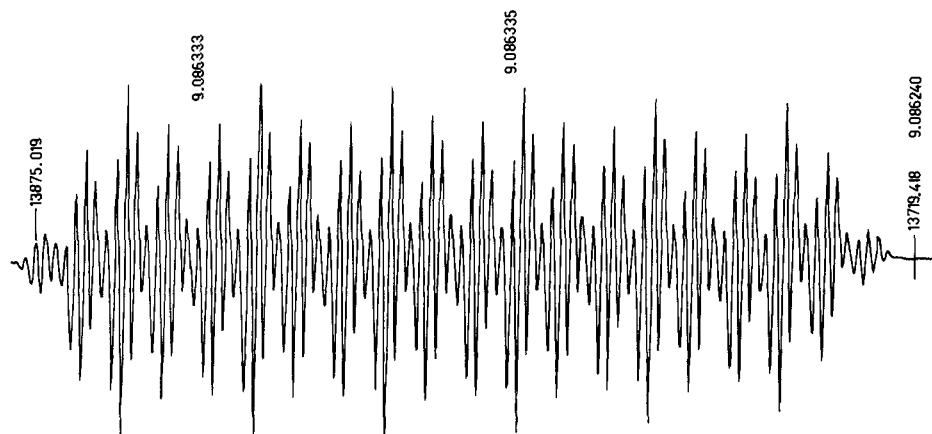


Figure 1. ESR spectrum of the adduct formed from decacarbonyldimanganese and 9,10-phenanthroquinone in benzene solution, showing resolved  $^{55}\text{Mn}$  and proton splittings.  $^1\text{H}$  NMR field markers are in kilohertz.

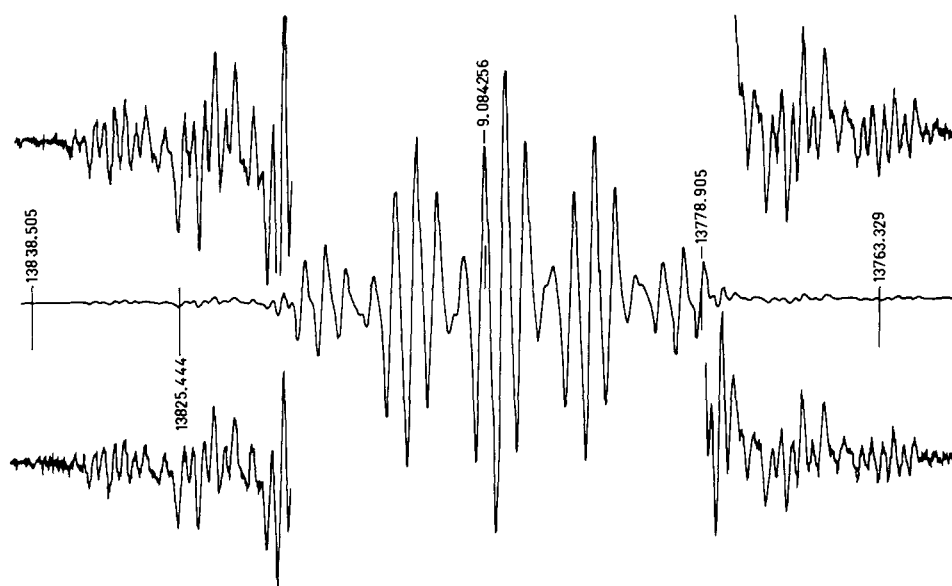
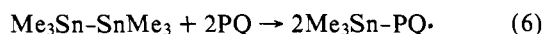


Figure 2. ESR spectrum of the trimethyltin adduct to phenanthroquinone in benzene solution. The insets show resolved  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  splittings at high gain.

tained at this temperature simply by irradiating the solutions, at the charge-transfer bands.

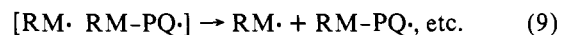
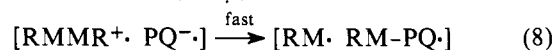
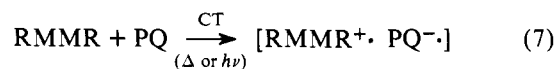
These results substantiate a general formulation, originally put forth by Kosower,<sup>2</sup> that electron-transfer processes resulting from charge-transfer interactions can share common photochemical and thermal pathways. More generally, we believe that organometals are desirable electron donors for the investigation of a variety of other charge-transfer processes. In a number of cases, the paramagnetic species can be observed directly. Thus, if a frozen solution of hexamethylditin and 9,10-phenanthroquinone (PQ) in benzene, prepared at  $-150^\circ\text{C}$  in the dark, is allowed to warm in the cavity of an ESR spectrometer, the intense ESR spectrum of the adduct,  $\text{Me}_3\text{Sn-PQ}\cdot$ , is observed:<sup>3</sup>



Under comparable conditions  $(\text{CH}_3)_3\text{Pb-Pb}(\text{CH}_3)_3$ ,  $(\text{OC})_5\text{-Mn-Mn}(\text{CO})_5$ , and  $(\text{CH}_3)_3\text{Sn-Mn}(\text{CO})_5$  afford paramagnetic adducts,  $(\text{CH}_3)_3\text{Pb-PQ}\cdot$ ,  $(\text{OC})_5\text{Mn-PQ}\cdot$ , and  $(\text{CH}_3)_3\text{Sn-PQ}\cdot$ , respectively, showing well-resolved and characteristic ESR spectra in Figures 1 and 2.

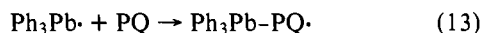
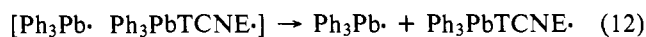
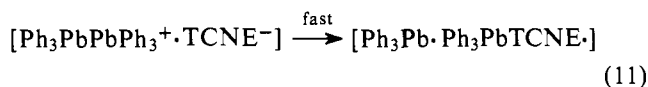
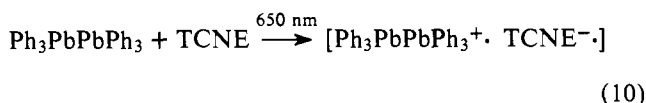
The thermal reaction between hexaphenyldilead and phenanthroquinone to afford  $\text{Ph}_3\text{Pb-PQ}\cdot$  in benzene solution is slow, as is the reaction with tetraethyllead. However, upon

irradiation through a Pyrex filter, the ESR spectrum of the adducts can be observed immediately. Since hexaphenyldilead is transparent in this region of the spectrum, it is unlikely that the adduct  $\text{Ph}_3\text{Pb-PQ}\cdot$  is formed by photolysis of the Pb-Pb bond.<sup>4</sup> As an alternative, we suggest that a charge-transfer (CT) process, which is both thermally and photochemically accessible, leads to the paramagnetic organometal adducts of PQ in the following manner:



The participation of a charge-transfer process can be shown in the following way.<sup>5</sup> Hexaphenyldilead and PQ do not produce the adduct  $\text{Ph}_3\text{Pb-PQ}\cdot$  upon irradiation with visible light between 350 and 650 nm (using a monochromator at 50-nm intervals). A mixture of TCNE and  $\text{Ph}_3\text{Pb-PbPh}_3$  in benzene shows an intense, yellow charge-transfer band with  $\lambda_{\text{max}} \sim 300$  nm,<sup>6</sup> but strongly tailing out beyond 650 nm. Addition of PQ to the solution causes no apparent thermal change at room temperature in the dark. However, irradiation at 650 nm af-

fords  $\text{Ph}_3\text{Pb-PQ}\cdot$ , though not so strongly as that obtained by irradiation at 300–350 nm in the absence of TCNE. A charge-transfer process similar to that above, but photochemically pumped, is shown below:



According to this scheme,  $\text{Ph}_3\text{Pb} \cdot$  results from the photoinduced electron transfer from  $\text{Ph}_3\text{Pb-PbPh}_3$  to TCNE in eq 10, followed by the rapid collapse of the ion pair.<sup>7</sup> Furthermore, diffusion of  $\text{Ph}_3\text{Pb} \cdot$  must be sufficiently competitive with cage combination to allow the formation of  $\text{Ph}_3\text{Pb-PQ} \cdot$  in eq 13.

Thus, there is a common theme of charge-transfer interactions, induced thermally and photochemically, leading to facile reactions of organometals. The chemically induced dynamic magnetic polarization studies, both CIDNP and CIDEP, presently in progress will shed further light on the mechanistic details of these interesting processes. Furthermore, in addition to quinones and TCNE, a variety of other compounds, especially organic halides and carbonyl compounds, are known to act as electron acceptors, and many types of organometals other than alkyl metals are also available as electron donors. We hope that these studies will aid in the further development of general concepts related to the activation of organometals, especially as intermediates in reactions with organic substrates.

## References and Notes

- (1) (a) H. C. Gardner and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 2460 (1976). (b) J. Y. Chen, H. C. Gardner, and J. K. Kochi, *ibid.*, **98**, 6150 (1976).
- (2) E. M. Kosower, *Prog. Phys. Org. Chem.*, **3**, 81 (1965).
- (3) The spin adducts of organometal radicals  $\text{RM} \cdot$  to 9,10-phenanthroquinone have the general structures shown (K. S. Chen, J. K. S. Wan, and J. K. Kochi,



unpublished work). For the  $\text{Me}_3\text{Sn}$  adduct,  $g = 2.0030$  and the hyperfine splittings are 8.75 ( $^{119}\text{Sn}$ ), 8.36 ( $^{117}\text{Sn}$ ), 1.87 (quintet) and 0.43 (quintet) (H) G. For the manganese carbonyl adduct,  $g = 2.0028$  and the hfs are 5.50 ( $^{55}\text{Mn}$ ) and 1.72 (quintet) and 0.40 (quintet) (H) G. Both adducts are formed simultaneously from  $\text{Me}_3\text{Sn-Mn}(\text{CO})_5$ .

- (4) In this experiment energy transfer from  $\text{PQ}^*$  cannot be eliminated since PQ has a weak absorption in this region.
- (5) Cf. also N. S. Vyazankin, V. T. Bychkov, O. V. Linzina, L. V. Aleksandrova, and G. A. Razuvaev, *J. Organomet. Chem.*, **31**, 311 (1971). G. A. Abakumov, E. N. Gladyshev, N. S. Vyazankin, G. A. Razuvaev, P. Ya. Bayushkin, and V. A. Muraev, *ibid.*, **64**, 327 (1974).
- (6) The maximum is obscured by the end absorption of hexaphenyldiiodole.
- (7) Cation radicals formed in eq 2 and 7 are highly unstable to homolysis. For example,  $\text{Ph}_3\text{Pb-PbPh}_3^+ \cdot \rightarrow \text{Ph}_3\text{Pb} \cdot + \text{Ph}_3\text{Pb}^+$  (see A. Peloso, *J. Organomet. Chem.*, **67**, 423 (1974)) and  $\text{R}_4\text{Sn}^+ \cdot \rightarrow \text{R}_3\text{Sn}^+ + \text{R} \cdot$  (see H. C. Gardner and J. K. Kochi, *J. Am. Chem. Soc.*, **97**, 1855 (1975)). Consequently the ion pair may collapse to form either a new ion pair as in eq 3 or a radical pair as in eq 8. The latter is favored for dimetals (i.e.,  $\text{RMMR}^+$ ), whereas the high reactivity of alkyl radicals suggests that an  $\text{R}_4\text{M}^+$  collapses as in eq 3.
- (8) We wish to thank the National Research Council of Canada and the National Science Foundation for financial support.

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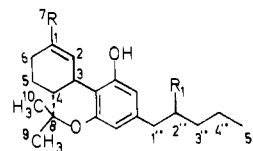
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## A Terpenic Synthron for $\Delta^1$ -Cannabinoids<sup>1</sup>

Sir:

The reversal of the reactivity (i.e., umpolung) of carbonyl compounds when masked as dithioacetals has been shown to be of use for the elaboration of organic molecules.<sup>2</sup> We have applied this principle to the synthesis of metabolites of  $\Delta^1$ -tetrahydrocannabinol (THC, **1**) by preparing the novel *cis*-



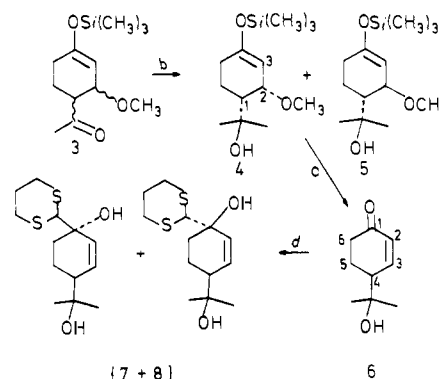
1	R = CH <sub>3</sub>	R <sub>1</sub> = H
2	R = COOH	R <sub>1</sub> = OH
14	R = CHO	R <sub>1</sub> = H
15	R = CH <sub>2</sub> OH	R <sub>1</sub> = H

and *trans*-terpenes **7** and **8**, which contain the dithiane masking group, and condensing them with olivetol under acid catalysis. Interestingly, by introducing the dithiane moiety into the THC structure, isomerization of the normally<sup>3</sup> labile  $\Delta^1$  unsaturation to the  $\Delta^6$  isomer is effectively inhibited. In light of the fact that the metabolites of  $\Delta^1$ -THC also possess this unstable double bond, these versatile dithiane-containing terpenes have great potential as synthons for a variety of hitherto inaccessible metabolites that have been oxidized at C<sub>7</sub> and on the C<sub>5</sub> side chain (e.g., **2**).<sup>3</sup> The synthesis and transformation of these terpenes and the nature of the interactions between the dithiane nucleus and the neighboring double bond are described below.

Treatment of the Diels-Alder adduct<sup>4</sup> (**3**, Scheme I) of *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene and methyl vinyl ketone with a 10% molar excess of  $\text{CH}_3\text{MgI}$  afforded, after chromatography (1:1 ether-petroleum ether), equal amounts of compounds **4** and **5** as colorless liquids (99%).<sup>5</sup>

The unsaturated ketone (**6**, 43%)<sup>6</sup> was obtained by hydrolyzing a mixture<sup>7</sup> of **4** and **5** with 2% trichloroacetic acid in  $\text{CCl}_4$  at reflux.<sup>8</sup> Addition of the lithium anion of 1,3-dithiane to this ketone occurred exclusively in a 1,2 fashion<sup>9</sup> and furnished a mixture<sup>10</sup> of the desired terpenes **7** and **8**, which were separated by gradient elution on Florisil (ethyl acetate-benzene). The first of these isomers to elute (41%, mp 116–117 °C)<sup>11a</sup> was allowed to react with 1.1 equiv of olivetol in the presence of 0.1 equiv of *p*-toluenesulfonic acid (*p*-TSA) in refluxing benzene for 15 min (Scheme II).<sup>11b</sup> A mixture was obtained from which THCs **9** (20%) and **10** (30%) were isolated by chromatography (graded ether-petroleum ether

Scheme I<sup>a</sup>



<sup>a</sup> All compounds are racemic. <sup>b</sup>  $\text{CH}_3\text{MgI}$  (1.1 equiv). <sup>c</sup>  $\text{Cl}_3\text{CCOOH}$ / $\text{CCl}_4$ , reflux. <sup>d</sup> 1,3-Dithiane, BuLi, THF, -30 °C.