Scheme I

$$[(\text{allyl})\text{NiBr}] + \text{RX} \longrightarrow \text{RX}\cdot^{-} + [(\text{allyl})\text{NiBr}]\cdot^{+} \quad \text{(a)}$$

$$\text{RX}\cdot^{-} \longrightarrow \text{R}\cdot + \text{X}^{-} \quad \text{(b)}$$

$$\text{R}\cdot + [(\text{allyl})\text{NiBr}] \longrightarrow \text{R-allyl} + \text{NiBr}\cdot \quad \text{(c)}$$

$$\text{NiBr}\cdot + \text{RX} \longrightarrow \text{RX}\cdot^{-} + \text{NiBr}^{+} \quad \text{(d)}$$

Scheme II

$$\text{R}\cdot + [(\text{allyl})\text{NiBr}] \longrightarrow [\text{R}(\text{allyl})\text{NiBr}]^{\cdot}$$

$$[\text{R}(\text{allyl})\text{NiBr}]^{\cdot} + \text{RX} \longrightarrow [\text{R}(\text{allyl})\text{NiBrX}] + \text{R}\cdot$$

$$[\text{R}(\text{allyl})\text{NiBrX}] \longrightarrow \text{R-allyl} + \text{NiBrX}$$

tion, π-(2-methoxyallyl)nickel bromide[4] was treated with (S)-(+)-2-iodooctane ($[\alpha]^{25}{}_{589}$ +42.2°).[5] The resulting 4-methyl-2-decanone was *completely racemic* by comparison with authentic (R)-(+)-4-methyl-2-decanone prepared by an independent method.[6] Racemization occurred in the product-forming step, since (R)-(+)-4-methyl-2-decanone ($[\alpha]^{25}{}_{589}$ +1.28°) was not racemized by subjection to the conditions of the reaction and isolation and, when the reaction was run to 30% completion, unreacted (S)-(+)-2-iodooctane was recovered without loss of rotation. Furthermore, this reaction was *completely inhibited* by the addition of less than 1 mol % m-dinitrobenzene, a potent radical anion scavanger.[7,8]

To test if inhibition by m-dinitrobenzene was general π-(2-methallyl)nickel bromide was treated under identical conditions[9] with 2-iodooctane, iodobenzene, β-bromostyrene, and methallyl bromide both in the absence and presence of 1 mol % m-dinitrobenzene. With 2-iodooctane, iodobenzene, and β-bromostyrene the uninhibited reactions went essentially to completion, while those containing inhibitor went only to the extent of 5–10% completion. With the highly reactive methallyl bromide, the reaction containing inhibitor went to 50% completion. Thus inhibition of this reaction by very small amounts of radical anion scavanger appears to be general and is strongly suggestive of a radical chain process.

A mechanism consistent with the above observations for the alkyl, aryl, and allyl halides is presented in Scheme I.

One possible chain initiation step (a) involves electron transfer from the nickel complex to the halide to produce the corresponding radical anion.[10] The chain carrying steps (b–c) are similar to those proposed by Kornblum[7a,b] and Russell[7c] for the reaction of nitro carbanions with p-nitrobenzyl chloride. Loss of stereochemistry may result from the radical intermediate in steps b and c. Inhibition by m-dinitrobenzene can occur by scavenging either $\text{RX}\cdot^{-}$ or $\text{NiBr}\cdot$. An alternative scheme for steps c, d, and b involves a free radical oxidative addition similar to that proposed by Osborn (Scheme II).[11]

While the reaction of β-bromostyrene with π-allylnickel halide complexes is also strongly inhibited by the presence of small amounts of m-dinitrobenzene, the stereochemistry of the double bond is maintained.[4] Thus, while this reaction also appears to be a radical chain reaction, it must differ somewhat in mechanism from the other cases discussed, since free vinyl radicals rapidly lose their stereochemistry.[12]

In contrast to the alkylation of organic halides and tosylates by diorganocuprates, for which a compelling case for an S_N2 mechanism has been made,[13] an electron transfer–radical chain mechanism best accommodates the observations reported above. The role of radical chain processes in other organometallic reactions as well as the use of radical initiators to effect the reaction of organometallic complexes with normally unreactive substrates are under current investigation.[14]

Acknowledgment. Support for this research through grants from the National Institutes of Health (CA 15529-01) and the National Science Foundation (GP-43626) is gratefully acknowledged.

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(8) This reaction was also inhibited by duroquinone, but larger amounts (10%) were required.

(9) The reaction of π-allylnickel halide complexes were carried out as described in ref 2a and 4. With each substrate studied two parallel reactions were set up and run under identical conditions with the exception of the addition of 1 mol % of m-dinitrobenzene to one of the reactions. When the uninhibited reaction was complete (color change from red to green) both reactions were quenched and the products isolated. The per cent of reaction was determined by integration of appropriate peaks in the nmr spectrum of the crude products. In all cases, >90% material balance was obtained, and the crude material consisted essentially of starting material and product. All products were identified by comparison with authentic material.

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(13) C. R. Johnson and G. A. Dutra, *J. Amer. Chem. Soc.*, **95,** 7783 (1973).

(14) After submission of this article, Osborn and coworkers reported that oxidative additions of alkyl halides to Pt(0) complexes involves a radical chain mechanism. In this system aryl, vinyl, and allyl halide reactions are not inhibited by radical scavengers: A. V. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, *J. Amer. Chem. Soc.*, **96,** 7146 (1974). Although scavenging of free radicals is proposed there it may be noted that the particular scavengers employed, duroquinone and galvinoxyl, could also inhibit *via* redox processes of the type suggested here.

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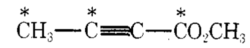
Received September 28, 1974

Signs of Long-Range Carbon–Carbon Coupling Constants. Tri-^{13}C-Labeled Tetrolic Ester

Sir:

With a spin of ½ and with no nonbonding valence electrons, ^{13}C is the nucleus expected to be most like ^{1}H in nmr spin-spin coupling. Indeed, for geometrically equivalent systems, long-range carbon–proton and proton–proton couplings appear to be correlated;[1] the ratio $J_{\text{CH}}/J_{\text{HH}}$ is +0.4 to +0.7.[2] To test the idea that this analogy may be extended to carbon–carbon couplings, one should determine long-range J_{CC} values, including signs, of a system that can be related to a geometrically equivalent carbon–proton system. We wish to report the successful determination of the signs of long-range carbon–carbon couplings of methyl tetrolate (**1**) and to compare these couplings with analogous J_{CH} values of a geometrically equivalent system.



$$\overset{*}{\text{C}}\text{H}_3\text{—}\overset{*}{\text{C}}\equiv\text{C—}\overset{*}{\text{C}}\text{O}_2\text{CH}_3$$

1

Compound **1,** labeled with >90% ^{13}C at each of the positions C-1, C-3, and C-4, was synthesized in a 15-step scheme originating from >90% ^{13}C carbon dioxide.[3] The proton-decoupled carbon nmr spectrum of **1** exhibited a

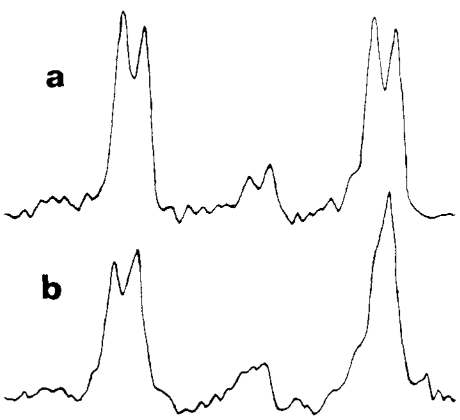


Figure 1. C-1 region of the proton-decoupled carbon nmr spectrum of **1**: (a) normal; (b) while high-field doublet of C-4 is selectively spin decoupled.

12-line AMX pattern arising directly from the three labeled carbons. The proton-decoupled spectrum was considerably more involved: C-3 and C-4, coupling with the H-5 protons (see Table I), each appeared as a quartet of doublets of doublets; C-1, coupling with the H-5 protons and the H-6 protons, appeared as a fairly complex but discernible doublet of multiplets (see Figure 2a). The absolute values of J_{CC} and J_{CH} involving the labeled carbons were directly measured (first-order patterns were exhibited), and then the signs of these J values were determined relative to the directly bonded $^1J_{CH}$ value, which is known to be positive.[4] Thus, the absolute signs of all these couplings were determined. These values, including signs, are given in Table I.

Four techniques were used to determine these relative signs: (1) proton-decoupled $^{13}C\text{-}\{^{13}C\}$ double resonance[5] (selective spin decoupling of J_{14} with observations of consequent collapse of doublets in the carbon spectrum); (2) proton-coupled $^{13}C\text{-}\{^{13}C\}$ double resonance[5] (selective spin decoupling of J_{14} with observations of consequent collapse of doublets in the carbon spectrum); (3) $^{13}C\text{-}\{^{1}H\}$ double resonance[5] (selective spin decoupling of J_{15} and J_{35} in the proton region, with observations of consequent collapse of multiplets in the carbon region); (4) the SPT approach (selective population transfer)[6] involving proton decoupled $^{13}C\text{-}\{^{13}C\}$ gated double resonance experiments where individual carbon transitions were irradiated with observation of consequent perturbations in the carbon region. All four techniques were used to determine the signs of the J_{CC} values, while techniques (2) and (3) were used to determine the signs of the J_{CH} values.

Figures 1 and 2 illustrate examples of spectral patterns observed in this study. Figure 1a shows the normal proton-decoupled region of C-1, a doublet of doublets; Figure 1b shows the same region while irradiating the high-field doublet of C-4 (this experiment shows J_{13} and J_{34} are of the same sign). Figure 2a shows the normal proton-coupled pattern of C-1; Figure 2b shows the same region while irradiating the highest field doublet of the proton region (this experiment shows J_{14} and J_{45} are of the same sign and J_{13} and J_{35} are of opposite sign).

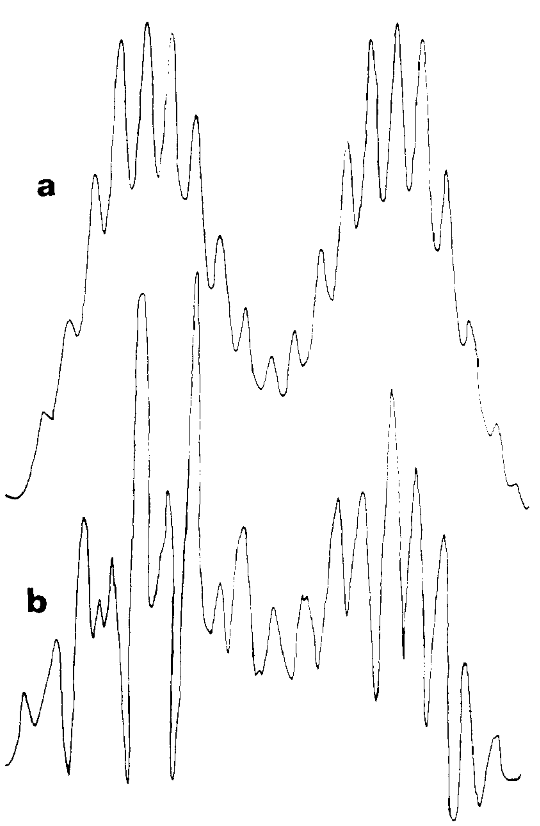
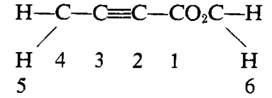


Figure 2. C-1 region of the proton-coupled carbon nmr spectrum of **1**: (a) normal; (b) while highest field doublet of proton region is selectively spin decoupled.

Below each value of J for **1** in Table I is given the analogous coupling of propyne (**2**), the model compound for **1** obtained by substituting the carboxyl group by a proton.[7] For those couplings whose nuclei are identical in **1** and **2**, the J values (including signs where available for **2**) agree: compare J_{34} (+65.15 and 67.4 Hz), J_{35} (−10.33 and −10.6 Hz), and J_{45} (+132.1 and +132.4 Hz). Comparing the analogous J_{CH} and J_{HH} values of **1** and **2** (J_{15}), the ratio J_{CH}/J_{HH} is +0.5 and thus lies in the anticipated range.[2] Finally, comparing the analogous J_{CC} and J_{CH} couplings (J_{14} and J_{13}), the ratio J_{CC}/J_{CH} also lies in this range of +0.4 to +0.7 (the ratio for J_{14} is +0.5 and for J_{13} is +0.4).[8]

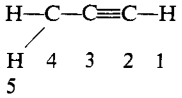
The success of this type of treatment would lead one to expect carbon–carbon couplings to compare in a similar fashion to geometrically equivalent proton–proton cou-

Table I. J_{CC}, J_{CH}, and J_{HH} Values (Hz) for **1** and **2**



$\mathrm{H_3\overset{*}{C}-\overset{*}{C}\equiv C-\overset{*}{C}O_2CH_3}$ (H-5 on C-4; H-6 on methyl)

1



$\mathrm{H_3C-C\equiv C-H}$ (carbons 4 3 2 1; H-5 on C-4)

2

Compound	J_{14}	J_{13}	J_{34}	J_{15}	J_{35}	J_{45}	J_{16}
1	+1.84	+20.33	+65.15	−1.48	−10.33	+132.1	(3.5)
2	+3.6[a]	+50.8[a]	67.4[b]	−2.93[c]	−10.6[a]	+131.4[a]	

[a] H. Dreeskamp, E. Sackmann, and G. Stegmeier, *Ber. Bunsenges. Phys. Chem.*, **67**, 860 (1963). [b] J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **94**, 6021 (1972). [c] G. Englert, A. Saupe, and J.-P. Weber, *Z. Naturforsch. A*, **23**, 152 (1968).

plings. Thus, the J_{CC}/J_{HH} ratio should be in the range of $+(0.4)^2$ to $+(0.7)^2$, or +0.16 to +0.49 (because $J_{CC}/J_{HH} = J_{CC}/J_{CH} \times J_{CH}/J_{HH}$). Indeed, the J_{CC}/J_{HH} ratio (for J_{14} of **1** and J_{HH} of acetylene[9]) is $+1.84/+9.53 = +0.2$.

Thus, in the acetylenic compound **1**, the J_{CC} values do compare with geometrically equivalent J_{CH} and J_{HH} values in the manner that J_{CH} values compare with geometrically equivalent J_{HH} values. Evidence therefore continues to accumulate that carbon-13 behaves as proton in nmr couplings and that couplings involving carbon-13 have similar mechanisms to those involving proton.

Work is continuing to determine J_{CC}/J_{CH}, including signs, for multiply labeled olefinic and aliphatic compounds.

Acknowledgments. The authors wish to express their gratitude to the Robert A. Welch Foundation, Houston, Texas (Grant B-325), to North Texas State University Faculty Research, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF 7409-AC4,6), for financial support of this work.

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(10) Robert A. Welch Foundation Predoctoral Fellow, 1971–1974.

(11) Petroleum Research Fund Postdoctoral Fellow, 1972–1974.

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Received September 21, 1974

Comment Regarding the Rate Constant for the Reaction between 1,3-Diphenylisobenzofuran and Singlet Oxygen

Sir:

Recently Matheson, *et al.*, stated[1] that the rate constant for reaction between 1,3-diphenylisobenzofuran (DPBF) and singlet oxygen (${}^1\Delta$) reported by ourselves,[2,3] and others,[4] is an order of magnitude too high and primarily reflects physical quenching of ${}^1\Delta$ by DPBF rather than reactive quenching. This assertion is supported neither by our own laser photolysis data nor by data from several other laboratories.

While DPBF no doubt physically quenches ${}^1\Delta$ to some extent, an analysis of photooxidation efficiencies leads us to rule out this process as a major decay pathway. Under the conditions of our experiments[3] the possible routes for ${}^1\Delta$ decay are

$$ {}^1\Delta \xrightarrow{1/\tau} {}^3\Sigma \text{ (solvent quenching)} \tag{1}$$

$$ {}^1\Delta + \mathrm{A} \xrightarrow{k_q} {}^3\Sigma + \mathrm{A} \text{ (physical quenching by acceptor A)} \tag{2}$$

$$ {}^1\Delta + \mathrm{A} \xrightarrow{k_a} \mathrm{AO_2} \text{ (reactive quenching)} \tag{3}$$

where A is DPBF in the present case. Since [A] does not change too drastically following a laser pulse, it is possible to derive the following expression to explain the observed bleaching of DPBF

$$[\mathrm{AO_2}]_{t=\infty} - [\mathrm{AO_2}]_t \simeq \frac{k_a[\mathrm{A}][{}^1\Delta]_{t=0}}{1/\tau + (k_q + k_a)[\mathrm{A}]} \cdot e^{-\{1/\tau + (k_q + k_a)[\mathrm{A}]\}t} \tag{4}$$

where $[\mathrm{AO_2}]_{t=\infty}$ is the concentration of products after complete decay of ${}^1\Delta$ and $[{}^1\Delta]_{t=0}$ is the concentration produced by the laser pulse. Substituting $[\mathrm{AO_2}] = 0$ at $t = 0$ and rearranging gives

$$[{}^1\Delta]_{t=0} = [\mathrm{AO_2}]_{t=\infty} \frac{1/\tau + (k_q + k_a)[\mathrm{A}]}{k_a[\mathrm{A}]} \tag{5}$$

In an earlier report[3] we assumed that the observed DPBF quenching constant, $(k_q + k_a)$, was approximately equal to k_a itself. Using the measured values of τ, k_a, and $[\mathrm{AO_2}]_{t=\infty}$ in methanol, we calculated that under suitable conditions (see Results, section 3 in ref 3) $[{}^1\Delta]_{t=0}$ was equal to 90 ± 10% of the concentration of sensitizer (Methylene Blue) triplets produced by a pulse. If, as Matheson and Lee suggest, $k_a \simeq 0.1(k_q + k_a)$, the quantum efficiency of ${}^1\Delta$ production from Methylene Blue Triplets would have to be ~9.0. In order not to exceed the generally accepted maximum quantum efficiency of 1.0, k_q must in fact be $\lesssim 0.1k_a$ justifying our above assumption.

The photolysis data of Adams and Wilkinson also support this conclusion.[5] Referring to Figure 3 in ref 5, it is evident that essentially all of the initial level of 5×10^{-5} *M* DPBF is bleached in a single laser pulse. The concentration of ${}^1\Delta$ produced by the pulse cannot exceed 10^{-4} *M*, the concentration of Methylene Blue sensitizer. If nine molecules of ${}^1\Delta$ were indeed quenched by DPBF for each which reacts, then at most only 1×10^{-5} *M* DPBF could be bleached. This limit is further reduced if competition by solvent quenching is included in the analysis.

Usui has measured quantum yields of photooxidation of DPBF (number of molecules oxidized per photon absorbed by Methylene Blue) in methanol.[6] Values near unity were obtained at DPBF concentrations as low as ~10^{-4} *M*. Again, if $k_a \simeq 0.1(k_q + k_a)$, then the quantum yield could never exceed 0.1.

Olmsted and Akashah[7] have used their quantum efficiency data and our τ value in methanol (which is accurate regardless of the relative magnitudes of k_q and k_a) to calculate a value of k_a for DPBF of 6.13×10^8 M^{-1} sec^{-1} quite close to our value of 8×10^8 M^{-2} sec^{-1}. Reactive and physical quenching are unambiguous here as in the other efficiency measurements.