

Figure 2. (a) First-derivative ESR spectra of the DTBQ-Re(CO)₄ radical complexes in toluene at various temperatures; (b) second-derivative ESR spectrum of the same radical complex at 60 °C.

345 and 705 nm. This suggests that the planarity of the quinone moiety has been retained in the radical complex. As a comparison the emission spectrum of the parent DTBQ has band centers at 335 and 665 nm.

Comparison of the IR spectrum of the DTBQ-Re(CO)₄ radical complex with those of the starting compounds (in KBr pellets) suggests that the carbonyl groups of the *o*-quinone have been drastically altered, whereas the carbonyl groups originally complexed to the rhenium retain much of their original character upon radical formation. This is inferred from the observation that the carbonyl stretch of the quinone at 1650 cm⁻¹ completely disappears from the IR spectrum of the radical, while the carbonyl absorption region of Re₂(CO)₁₀ at ~2000 cm⁻¹ changes very little. The C-H stretching region is very similar in both the parent quinone and the rhenium-quinone radical complex, which supports the assignment of the DTBQ-Re(CO)₄ radical as having a planar quinone moiety with the Re complexing symmetrically to the two quinone oxygen atoms.

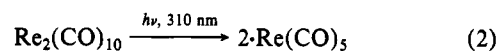
The first-derivative ESR spectrum of the radical complex at various temperatures is shown in Figure 2. The second-derivative spectrum at 60 °C, also shown in Figure 2, clearly exhibits the proton hyperfine splitting of 3.46 G, which by analogy to the uranyl-DTBQ complex⁴ is assigned to the proton between the two *tert*-butyl groups on the quinone ring. The *g* factor of the DTBQ-Re(CO)₄ radical complex was measured to be 2.003. The "average" Re hyperfine coupling constant is 28.2 G; the two isotopes of ¹⁸⁵Re (37.05%, *I* = 5/2) and ¹⁸⁷Re (62.93%, *I* = 5/2) could not be resolved, as their magnetic moments differ only by 1%. The low *g* factor of the radical complex is expected and is probably due to the large spin-orbit coupling of the Re atom.

A number of related diketone-rhenium carbonyl radical complexes have also been prepared and studied in our laboratory. These include the furil-rhenium carbonyl, the *o*-naphthoquinone-rhenium carbonyl, the tetrachloro-*o*-quinone-rhenium carbonyl, the tetrabromo-*o*-quinone-rhenium carbonyl, and the di-*tert*-butyl azodicarboxylate-rhenium carbonyl radical complexes. Two unusual features common to the ESR spectra of the rhenium radical complexes are the symmetrical broadening of the pair of lines corresponding to *m*_l = 3/2 and the slightly unequal

spacings among the rhenium lines, with the splittings at the high-field half being about 5% greater than the corresponding low-field half. These features are due to second-order effects, including both nuclear hyperfine and quadrupole coupling effects. A detailed ESR investigation of the rhenium-quinone radical complexes and other group 7B metal-ketone radical complexes is in progress.

The unique property of the DTBQ-Re(CO)₄ (and other related ketone-rhenium complexes) radical is its extraordinary thermal stability. Even at high temperatures up to 80 °C, the radical complexes do not decay significantly. Planned experiments include both X-ray and ¹³C NMR characterization of these interesting quinone-rhenium radical complexes.

Finally, the results also shed some light on the mechanism of the photoreaction of quinone and the rhenium carbonyl. If the benzene solution containing both reactants was irradiated at the *n*,π* band of the *o*-quinone at 395 nm, no reaction was observed. However, if the photolysis was carried out at 310 nm, which is associated with the σ_b → σ* band of the Re₂(CO)₁₀, the solution immediately turned red with the formation of the DTBQ-Re(CO)₄ radical complex. This is consistent with the following reaction mechanism:



The escape of CO from the solution during photolysis was also observable. In the present system, a photochemical charge transfer mechanism between Re₂(CO)₁₀ and DTBQ is unlikely, as quinone is not the photoactive reactant here and the quinone radical anion was not observed during the reaction.

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An NMR Technique for Tracing Out the Carbon Skeleton of an Organic Molecule

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We propose a new method of establishing the connectivity of the carbon skeleton of an organic molecule, the first and most important step in a complete structural determination. The technique is based on an earlier NMR experiment^{1,2} for studying carbon-13-carbon-13 spin-spin coupling which uses the momentary creation of double-quantum coherence³⁻⁵ to suppress the strong signals from isolated carbon-13 spins and reveal the weak carbon-13 satellite spectrum. If the magnitudes of the coupling constants are sufficiently well differentiated, they may be assigned to specific pairs of carbon resonances simply by picking out the repeated splittings. Adjacent carbon sites are thus identified directly. However, in many cases the molecular framework is too complex for this simple method to be applicable—each carbon site can have up to four directly bonded neighbors, and the carbon-carbon splittings may be close in magnitude or not clearly resolved. Consequently an *independent* method of assignment is needed.

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Table I. Comparison of the Observed and Predicted Double-Quantum Frequencies of 5 α -Androstane

carbon site	obsd freq, ^a Hz	pred freq, Hz
9	352, 1107	+353, +1110, +1132
14	564, 1091	+565, +1089, +1335
5	366, 366, 728	+365, +365, +729
13	537, 545, 1335	-535, +546, +620, +1335
17	403	-401, +620
12	456, 545	-457, +546
1	314, 398	+312, -399
10	313, 728, 1131	+312, +729, -1027, +1132
8	25, 1091, 1110	-25, +1089, +1110
7	25, 364	-25, -367
4, 6	366, 366, 366, 656	+365, +365, -367, -654
3	656, 1002	-654, -1001
15	566, 1158	+565, -1156
2	399, 1001	-399, -1001
11	354, 457	+353, -457
16	402, 1156	-401, -1156
18		-535
19		-1027

^a Signs not determined.

Examination of several possible methods of identifying coupled carbon-13 spins suggests that the procedure which promises the highest sensitivity is one which uses the frequency of the double-quantum coherence itself as the criterion for connectivity. In natural-abundance samples, the carbon-13 satellite spectra are of the AX (or AB) type, provided that the protons are decoupled. A two-dimensional Fourier transform experiment⁶ is performed in which both A and X carry information about the double-quantum frequency,⁴ thus identifying them as part of the same coupled spin system. The double-quantum frequency occurs at the algebraic sum of the two chemical shifts (measured with respect to the transmitter frequency).

Experiments were carried out at 50 MHz on a Varian XL-200 spectrometer modified for two-dimensional spectroscopy, using the pulse sequence $T-90^\circ-\tau-180^\circ-\tau-90^\circ-t_1-90^\circ$ -acquisition (t_2). Wide-band proton decoupling was used throughout. For first-order spin coupling, optimum conversion into double-quantum coherence⁷ requires that $\tau = 1/(4J_{CC})$, in practice, 7 ms. The double-quantum coherence evolves during t_1 and is reconverted into transverse nuclear magnetization by the last 90° pulse, which is cycled in phase in 90° steps. A similar cycling of the phase of the receiver in the opposite sense suppresses the signals from isolated carbon-13 spins.^{1,8,9} After two-dimensional Fourier transformation, a spectrum is obtained with the conventional carbon-13 satellite lines in the F_2 dimension and the corresponding double-quantum frequencies in the F_1 dimension.⁴ The range of double-quantum frequencies can be minimized by setting the transmitter frequency near the center of the conventional spectrum, using quadrature detection.

Directly coupled carbon-13 resonances are identified by the fact that they generate the same double-quantum frequency. Figure 1 shows a series of F_1 traces extracted from the two-dimensional spectrum of 5 α -androstane (**1**). This spectrum was obtained in

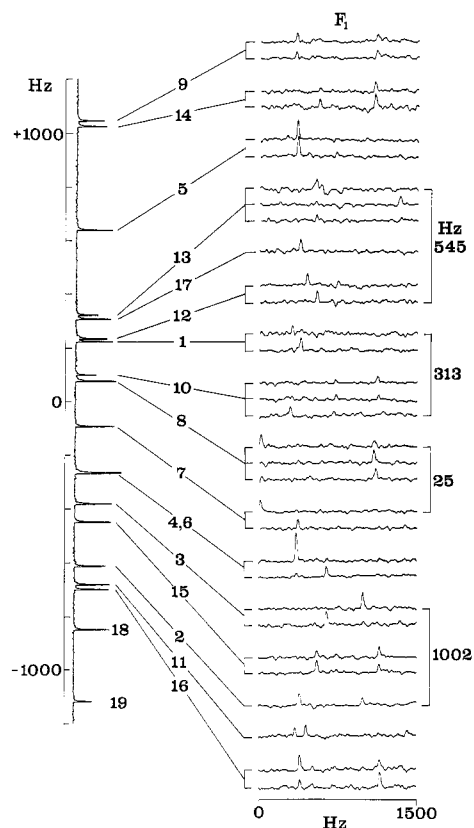
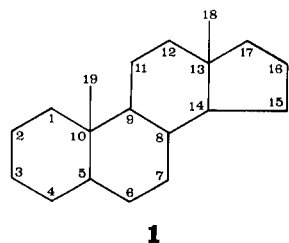


Figure 1. Traces extracted from the two-dimensional carbon-13 spectrum of 5 α -androstane, showing the double-quantum transitions in the F_1 dimension and their relationship to the resonances of the conventional spectrum (left-hand edge). A common frequency of 545 Hz may be observed in traces from sites C_{12} and C_{13} ; three other examples are shown, linking sites C_1 and C_{10} , C_7 and C_8 , and C_2 and C_3 . Sensitivity was too low to detect the double-quantum transition from the methyl groups C_{18} and C_{19} . The resulting assignment is in agreement with that of Eggert and Djerassi.¹²

10 h from a 1.5 M solution. Four examples are given where the same double-quantum frequency is recognized in traces from two different carbon sites, thus establishing the connectivity of C_{12} and C_{13} (double-quantum frequency 545 Hz), C_1 and C_{10} (313 Hz), C_7 and C_8 (25 Hz), and C_2 and C_3 (1002 Hz). Note that a given carbon-13 resonance may be directly coupled to one, two, three, or four others. A comparison of the observed and predicted double-quantum frequencies is made in Table I. Of the 44 possible double-quantum frequencies, 37 were detected unequivocally. Coupling between methyl and quaternary carbons is particularly difficult to detect when both sites have long spin-lattice relaxation times; in principle, the preparation period T could be increased to optimize these responses. Poor sensitivity is also encountered for strongly coupled AB systems unless the timing parameter τ is specifically adjusted for this case.¹⁰

In these experiments the *sign* of the double-quantum frequency is not determined because the F_1 dimension is obtained by Fourier transformation of an amplitude-modulated signal. A later modification¹¹ of the pulse sequence permits the generation of a phase-modulated signal, thus discriminating between positive and negative F_1 frequencies. This additional information could be critical in certain circumstances.

While the earlier experiment¹ established a practical method of measuring single-bond carbon-carbon coupling constants, the present technique provides an independent method of assignment to specific pairs of carbon atoms. This direct, step-by-step recognition of adjacent sites lends itself particularly well to com-

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puter-based schemes for establishing the topology of the molecular framework. If necessary, this connectivity information could be supplemented by similar measurements based on long-range couplings.² We suggest that the proposed technique could be a powerful aid to structure determination in cases where specific isotopic enrichment is not feasible.

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The Principle of Cooperativity in Asymmetric Induction: A Demanding Test for Concertedness

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The requirement for orbital symmetry conservation in concerted reactions is such a powerful and general one ("Violations. There are none!")¹ that its scope has been extended through topological considerations to a host of systems which lack formal symmetry but whose stereochemistry indicates concert.² More recently, the existence of concertedness at all has been questioned by a revisionist school which has invoked instead a relative rate effect which produces the stereospecific fingerprint of concertedness only through the fast collapse of intermediate biradicals.³ Attempts to resolve this controversy have relied largely on circumstantial kinetic data, particularly the existence of large negative activation entropies. We now report the use of chiral prosthetic groups as direct probes of the geometry of the transition state of the Diels-Alder reaction and demonstrate that the cooperativity in asymmetric induction achieved is a direct result of the concertedness of the reaction.

Controversy surrounding the Diels-Alder reaction hinges on whether the incipient σ bonds are formed simultaneously or sequentially. The essential distinguishing feature of the two mechanisms is the nonequivalence of the two ends of the dienophile for the nonconcerted mechanism and the equivalence of the two ends for the concerted mechanism. Our approach was to probe for the geometry of the transition state by using one or two chiral groups at the ends of the dienophile and to test for the degree of asymmetric induction induced in each case. As a test case, we chose the cycloaddition of 1,3-diphenylisobenzofuran to dialkyl fumarates. The geometry of the transition state for the concerted reaction is illustrated in Figure 1. The two alkyl moieties are held sufficiently far apart by the rigid fumarate backbone that they can rotate independently. One becomes the exo substituent, the other endo. We now consider the effect on the transition state leading to enantiodifferentiation of replacing one, then two, methyl groups with an *l*-bornyl group. First, for the concerted reaction the differences in activation enthalpies for enantiodifferentiation when two chiral groups are present should be the arithmetic sum of differences for the individual chiral groups. This is analogous to additivities in isotope effects for a similar system.⁴ Second, the entropy contribution, which is often more important in determining asymmetric induction,⁵ will be given by $R \ln (P_{\text{exo}}/P_{\text{endo}})$, where P_{exo} and P_{endo} are the probabilities for enantiodifferentiation for exo and endo singly substituted transition states. Since the entropic effects will also be additive, we have the important result

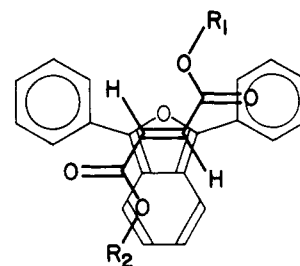
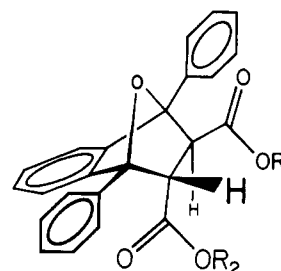


Figure 1. Diels-Alder transition state.



- 1, $R_1 = R_2 = \text{CH}_3$
 2 α , 2 β , $R_1 = R_2 = \text{bornyl}$
 3 α exo, 3 β exo, $R_1 = \text{bornyl}$, $R_2 = \text{CH}_3$
 3 α endo, 3 β endo, $R_1 = \text{CH}_3$, $R_2 = \text{bornyl}$

Figure 2. Cycloaddition products.

Table I. Chemical Shifts and Relative Intensities of Exo Protons

compound	chemical shifts, ppm (rel intens)
1	4.34
3 α , β (endo)	4.17 (0.47), 4.36 (0.72)
3 α , β (exo)	4.43 (0.71), 4.45 (1.0)
2 α , β (exptl)	4.25 (0.48), 4.48 (1.0)
2 α , β (calcd)	4.26 4.47

Table II. Product Ratios

3 α /3 β (endo)	3 α /3 β (exo)	2 α /2 β	
		exptl	pred
1.53	1.41	2.08	2.16

that the difference in activation free energies themselves will be additive and the relative rate of enantiomer formation k_{α}/k_{β} in the presence of two chiral groups will be the product of the rates in the presence of one chiral group (see eq 1). For the non-

$$\frac{k_{\alpha}}{k_{\beta}} = \frac{k_{\alpha 1}}{k_{\beta 1}} \frac{k_{\alpha 2}}{k_{\beta 2}} \quad (1)$$

concerted reaction, moreover, the lack of equivalence of the two ends implies that their energy effects on asymmetric induction will be nonadditive. We call this linear free energy relationship the principle of cooperativity in asymmetric induction. This concept is similar to the cumulative effects observed for methyl substitution on solvolytic reactions involving symmetric transition states.⁶ However, severe steric and electronic interactions introduce second-order effects which may prevent this relationship from holding rigorously in such cases.

The reaction of dimethyl fumarate with 1,3-diphenylisobenzofuran produced the Diels-Alder product 1 in quantitative yield. The reaction of dibornyl fumarate produced both diastereomers 2 α and 2 β in a 67:33 ratio, while the reaction of methyl bornyl fumarate gave a mixture of all four possible diastereomers 3 (see Figure 2). Fortunately, it was possible to relate the pair

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