(m, 13 H); ^{13}C NMR ($CDCl_3$) δ 55.3 (CH_3O), 104.1 (CO), 110.4, 116.4, 126.9, 127.5, 127.6, 127.8, 133.8, 141.5, 141.7, 144.9, 155.8.

Anal. Calcd for $C_{20}H_{16}O_3S$: C, 71.41; H, 4.80. Found: C, 71.63; H, 4.55.

Desulfination of Substituted Benzenesulfinamides (Sultines). Mercuridesulfination (Method A). General Procedure. Sulfinamide (250 mg) was dissolved in a mixture of 10 mL of NaOH (0.25 N) and 10 mL of ethanol. The mixture was refluxed for a few hours and acidified with acetic acid. Mercuric chloride (0.4 g) was added, and the mixture was refluxed for 1 h to give a precipitate. The precipitate was collected and suspended in a mixture of 10 mL of concentrated hydrochloric acid and 10 mL of ethanol. The mixture was refluxed for a few hours until the suspension dissolved. The mixture was diluted with water, extracted with benzene (3 × 25 mL), and dried over Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by recrystallization or chromatography on silica gel. Compounds (**16**–**18**) were prepared by this procedure.

***m*-Chlorophenyl phenyl sulfide (16)**: an oil from chromatography on silica gel (Et_2O–hexane) (lit.[31] bp 186 °C (30mm)); ^{1}H NMR ($CDCl_3$) δ 7.08–7.48 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 126.6, 127.8, 127.9, 128.3, 129.3, 129.9, 132.2, 133.8, 134.8, 138.8; MS *m/e* 220 (M^+, 100); MS (HR) for $C_{12}H_9ClS$ calcd 220.0113, found 220.0016.

(*m*-Chlorophenyl)diphenylcarbinol (17): oil (lit.[32] mp 53–55 °C); ^{1}H NMR ($CDCl_3$) δ 3.28 (b s, 1 H, ex), 6.85–7.36 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 81.6 (COH), 126.5, 127.5, 127.6, 127.8, 128.0, 128.4, 129.3, 129.5, 143.0, 145.9; MS (HR) for $C_{19}H_{15}ClNO$ calcd 294.0812, found 294.0815.

***m*-Tolyl phenyl sulfide (18)**: an oil from chromatography on silica gel (Et_2O–hexane); bp 309–310 °C (760 mm) (lit.[33] bp 309.5 °C (760 mm)); ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 7.15–7.58 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 21.2 (CH_3), 126.8, 127.9, 128.3, 128.9, 129.1, 130.7, 131.8, 135.2, 136.1, 138.9.

Desulfination of Substituted Benzenesulfinamides (Sultines). Hydrodesulfination (Method B). General Procedure. The sulfinamide (sultine) (250 mg) was dissolved in a mixture of 20 mL of NaOH (0.25 N) and 20 mL of ethanol and refluxed for a few hours with Raney Ni (5 g). The alkaline solution was filtered, acidified with 5% HCl, and extracted with chloroform. The extract was dried over Na_2SO_4 and evaporated to give the crude product, which was purified by recrystallization or chromatography on silica gel. Compounds **19** and **20** were prepared by the procedure described above.

***m*-Tolyldiphenylcarbinol (19)**: after recrystallization from benzene–petroleum ether, mp 65–67 °C (lit.[34] mp 62–65 °C); ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3 H), 2.78 (b s, 1 H, ex), 6.82–7.24 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 81.9 (COH), 125.2, 125.5, 127.1, 127.7, 127.8, 127.9, 128.4, 135.7, 137.5, 146.9.

(*m*-Methoxyphenyl)diphenylcarbinol (20): after recrystallization from ethyl ether, mp 88–89 °C (lit.[34] mp 87–89 °C); ^{1}H NMR ($CDCl_3$) δ 2.89 (b s, 1 H, ex), 3.74 (s, 3 H), 6.84–7.52 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 54.9 (OCH_3), 81.8 (COH), 120.5, 127.1, 127.6, 127.8, 127.9, 128.7, 128.6, 146.7, 148.4, 159.1.

Registry No. 5a, 14933-97-2; **5b**, 14934-01-1; **5c**, 6873-54-7; **5d**, 21532-54-7; **7a**, 123858-12-8; **7b**, 123858-13-9; **7c**, 123858-14-0; **7d**, 123880-76-2; **8a**, 123858-15-1; **8b**, 123858-16-2; **8c**, 123858-17-3; **8d**, 123858-18-4; **8e**, 123858-19-5; **8f**, 123858-20-8; **8g**, 123858-21-9; **9a**, 123858-22-0; **9b**, 123858-23-1; **9c**, 123858-24-2; **10a**, 123858-25-3; **11**, 66820-99-3; **12**, 123858-26-4; **13**, 123858-27-5; **14**, 123858-28-6; **15**, 123858-29-7; **16**, 38700-88-8; **17**, 29647-82-3; **18**, 13865-48-0; **19**, 6922-90-3; **20**, 78238-98-9; $(C_6H_5)_2CO$, 119-61-9; anisole, 100-66-3; thionylaniline, 1122-83-4.

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In Situ Generation of ^{17}O-Labeled Carbonyl Anion Radical Systems

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Strong well-resolved ESR spectra of ^{17}O-labeled anion radicals of ketones, quinones, and semidiones can be obtained via the simple addition of microliter amounts of 20% ^{17}O-labeled water to 0.5–1 mL of the unlabeled anion radical solutions in either hexamethylphosphoramide or in liquid ammonia. Compared to the standard procedure of synthesizing the labeled carbonyl compounds prior to the ESR study, this technique represents a very simple alternative procedure for the study of ^{17}O coupling constants and spin densities.

Introduction

The lack of a radioactive isotope of oxygen has been the source of frustration of life scientists interested in the aerobic process. On the other hand, ^{17}O does have a nuclear spin of 5/2 and can be studied in living systems via magnetic resonance techniques. Both in vivo and in vitro studies involving the direct observation of either the ESR or NMR ^{17}O coupling are hindered by the low natural abundance of ^{17}O (0.037%) and the difficulty in incorporating it into the systems of interest. However, the presence of ^{17}O-enriched water in biological systems can be observed indirectly via its effect upon water proton relaxation rates ($1/T_2$).[1] Of possible clinical value is the fact that the rate at which $1/T_2$ varies with the concentration of $H_2{}^{17}O$ is dependent upon the physiological and pathological state of the tissue.[1] The change in T_2 resulting from $H_2{}^{17}O$ enrichment is a function of the ^{17}O residence time, and it can even be used to study proton transfer rates.[2]

In contrast to the indirect effects of ^{17}O upon magnetic resonance parameters, the direct ESR observation of ^{17}O requires incorporation of this isotope of oxygen directly into the radical of interest. Besides radicals of biological interest, ^{17}O-enriched systems are needed for oxygen spin density,[3] ion association,[4] and hydrogen bonding[5] studies.

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[2] (a) Luz, Z.; Meiboom, S. *J. Am. Chem. Soc.* **1964**, *86*, 4768. (b) Luz, Z.; Meiboom, S. *Ibid.* **1964**, *86*, 4766. (c) Luz, Z.; Meiboom, S. *Ibid.* **1964**, *86*, 4764.

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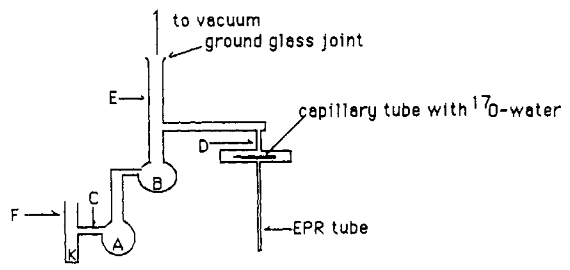


Figure 1. Apparatus used for the generation of the ^{17}O-enriched anion radical solutions. A few milligrams of the carbonyl compound to be reduced is placed into bulb B. After sealing at point F and evacuating the apparatus, the potassium metal is distilled from the side tube into bulb A. The solvent is then distilled directly into bulb B from the vacuum line, and the entire apparatus is sealed from the line at point E. The solution in bulb B is then poured into bulb A, where it is exposed to the metal mirror. A 0.5–1-mL portion of this anion radical solution is then poured into the EPR tube, which is subsequently sealed from the apparatus at point D. After recording the ESR spectrum, the sample can be agitated so as to break the capillary tube and liberate the $H_2{}^{17}O$. The EPR spectrum is then recorded again.

Oxygen spin densities are a sensitive function of the s–p interaction,[3] and for the case of ion association, it is well established that the oxygen atoms represent the site of anion radical–gegenion interaction in ion pairs involving ketyls, semidiones, and semiquinones.[4] Unfortunately, ^{17}O is very scarce, and the expense and time required to synthesize radical precursors greatly inhibit oxygen spin density studies.

The no-spin oxygen atoms in the anion radicals of carbonyl systems are readily replaced with ^{17}O by the simple addition of a few microliters of ^{17}O-labeled water to the anion radical solutions. The resulting reaction can be utilized to generate solutions of the ^{17}O-substituted radicals that yield strong well-resolved ESR spectra exhibiting the ^{17}O hyperfine splitting. With these oxygen couplings combined with the proton and ^{13}C couplings, there is a potential for obtaining a complete map of the spin density as a function of hydrogen bonding or ion association. This could be done even for those systems that normally have several "blind" oxygen atoms.

Experimental Section

Hexamethylphosphoramide (HMPA) and liquid ammonia solutions of carbonyl compounds were reduced to their ketyls, semidiones, or semiquinones under high vacuum on freshly distilled sodium or potassium mirrors in the apparatus shown in Figure 1. Representative samples (0.5–1 mL) of these solutions, for ESR analysis, were then poured into the ESR sample tubes which were sealed from the apparatus just above the perpendicular tube containing the $H_2{}^{17}O$ break tube. The ESR spectra were then recorded of the isotopically natural anion radicals. These tubes were then agitated horizontally so as to break the sealed tubes containing the $H_2{}^{17}O$, and after thorough mixing of the heavy water with anion radical solution, the ESR spectra were recorded again. In this manner we were able to record the well-resolved spectra for the ^{17}O-substituted anion radical of representative carbonyl systems that endure at room temperature.

Since the $H_2{}^{17}O$ is added to a very small volume of anion radical solution (0.5–1.0 mL of a ca. 10^{-3} M solution), the amount of this material required to carry out an experiment is very small (≈ 5 μL of 20% $H_2{}^{17}O$). The procedure will work just as well for anion radicals that are water sensitive as long as the amount of $H_2{}^{17}O$ added is not a large molar excess relative to the anion radical.

Samples of double ^{17}O-labeled benzoquinone ($C_6H_4{}^{17}O_2$) were synthesized via the method of Broz and Luz.[3] Thirty microliters of 20% $H_2{}^{17}O$ and 0.030 g of benzoquinone were dissolved in 3 mL of dioxane and sealed into a evacuated glass tube, which was heated to 80 °C for 24 h. After cooling, the tube was opened, and the dioxane was evaporated under reduced pressure. The water was extracted twice with ether, and the ether solution was dried with magnesium sulfate and filtered. The solid benzoquinones were sublimed and reduced to their anion radicals in liquid ammonia. ESR analysis of this solution at −75 °C proved it to contain three anion radicals: $C_6H_4O_2{}^{\bullet-}$, $C_6H_4{}^{17}OO^{\bullet-}$, and $C_6H_4{}^{17}O_2{}^{\bullet-}$ in a ratio of 160:20:1.0, respectively.

ESR spectra were recorded on a Bruker-IBM ER-200 spectrometer with a Bruker variable-temperature controller.

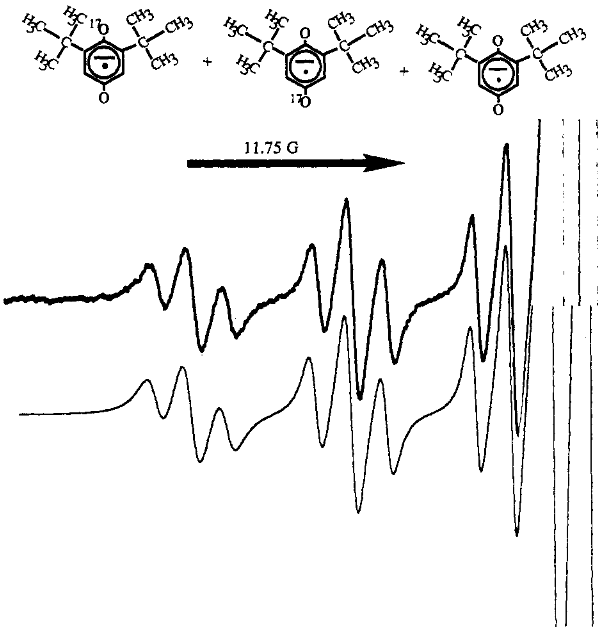
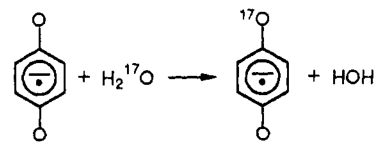


Figure 2. EPR spectrum of the liquid ammonia solution of 2,6-di-*tert*-butylsemiquinone (upper) after the addition of $H_2{}^{17}O$. The lines are broader than those for the unlabeled anion radical, which is off scale in this recording. The ^{17}O satellites increase in line width as: $m = -5/2 > -3/2 > -1/2$. The computer simulation (lower) generated by combining the spectrum of the 2,6-di-*tert*-butylsemiquinone system with an A_0 of 9.7 G and another with an A_0 of 7.5 G, along with the isotopically light anion radical spectrum.

Results and Discussion

When benzoquinone ($C_6H_4O_2$) is reduced with potassium metal in liquid ammonia a yellowish solution is generated, which yields the well-known five-line ESR pattern for the semidione (A_H = 2.42 G, 4 H's).[6] The addition of $H_2{}^{17}O$ to this anion radical solution results in the formation of the ^{17}O-substituted semiquinone, reaction 1, which is ESR



(1)

observable within 5 min after the addition. The signal for this isotopically heavy anion radical continues to grow at the expense of the isotopically light semidione for several minutes. The exchange of the ^{16}O with ^{17}O coupled with the relatively large ^{17}O splitting (A_0 = 9.42 G) results in the appearance of six miniature spectra of the semidione, most of which are located well outside of the field occupied by the isotopically light semidione. This allows the ^{17}O satellites to be scrutinized without interference.

Within 5 min after the addition of $H_2{}^{17}O$ to 2,6-di-*tert*-butylbenzosemiquinone in liquid ammonia the ESR signal of the ^{17}O-substituted anion radical can be observed

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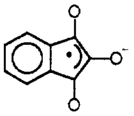
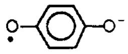
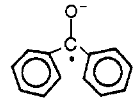
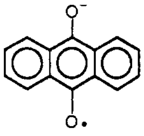
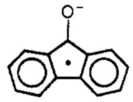
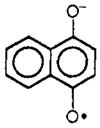
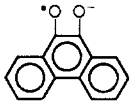
Table I. Oxygen-17 Hyperfine Coupling Constants in Gauss (Solvent, Temperature in Kelvin)

	3.94 (HMPA, 298) and 11.63 (HMPA, 298)		9.42 (NH_3, 205)
			8.25 (NH_3, 205)
	7.32 (NH_3, 205), 7.47 (HMPA, 298)		9.54 (HMPA, 298)
	9.15 (NH_3, 205)		8.08 (NH_3, 205)

well outside of the region of the isotopically light anion radial. Comparison of the spectra of the light and heavy anion radicals indicates that the ^{17}O-labeled material consists of two anion radicals, each with different ^{17}O couplings. These two splittings are so similar that they are not resolvable but result in line broadening of the ^{17}O satellites. This ESR signal is best simulated in terms of a mixture of three anion radicals: (1) the isotopically light system (A_H = 1.95 G for 2 protons); (2) an ^{17}O-substituted anion radical (A_H = 1.95 and A_o = 9.7 G); and (3) a second ^{17}O-substituted anion radical (A_H = 1.95 and A_o = 7.5 G). We assumed rapid exchange between the two different labeled anion radicals.

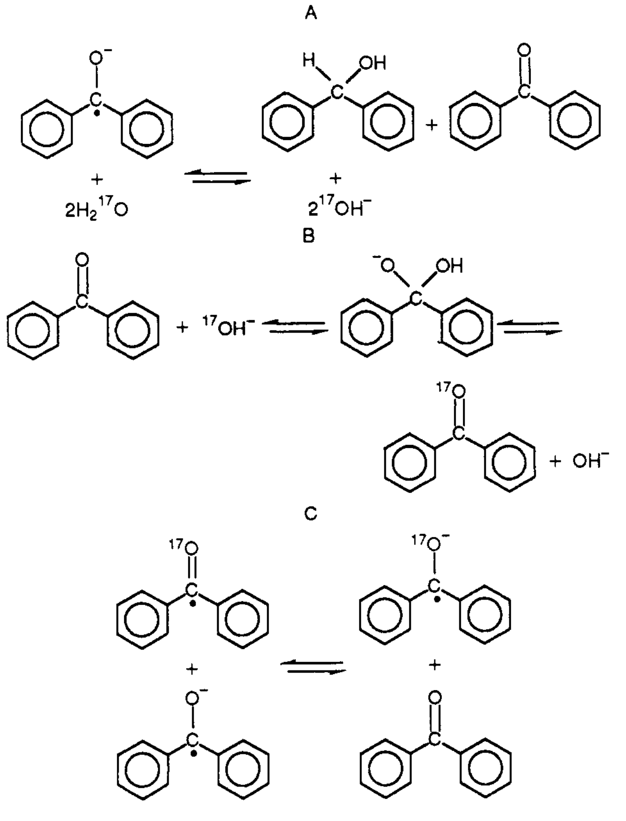
The reduction of a 1:2 molar mixture of 2,6-di-*tert*-butylbenzoquinone and $C_6H_4O_2$ results in the formation of a solution that exhibits both anion radicals simultaneously upon ESR analysis, and the addition of a molar deficient amount of $H_2{}^{17}O$ to this mixture results in the formation of all three of the possible ^{17}O-enriched semiquinones. However, in the absence of water, the reduction of a mixture of ^{17}O-enriched benzoquinone ($C_6H_4O^{17}O$) and normal 2,6-di-*tert*-butylbenzoquinone ($C_{14}H_{20}O_2$) does not result in the appearance of either of the ^{17}O-enriched 2,6-di-*tert*-butylbenzosemiquinones, and even after several days, the only ^{17}O anion radical present in solution is that of $C_6H_4O^{17}O$. Thus, any exchange of ^{17}O between anion radicals (reaction 2) is very slow.

$$C_6H_4O^{17}O^{\bullet-} + C_{14}H_{20}O_2 \rightarrow C_6H_4O_2 + C_{14}H_{20}O^{17}O^{\bullet-} \quad (2)$$

The oxygen exchange reaction (reaction 1) appears to be general for both semidiones and semiquinones. This is evidenced by the fact that ^{17}O-enriched anthrasemiquinone, naphthaquinone, and phenanthrasemidione can be generated by this technique in either liquid ammonia or HMPA (Table I). These two solvents are ideal for these studies, since they allow observation of the ESR spectra without hyperfine splitting from the counter ion.

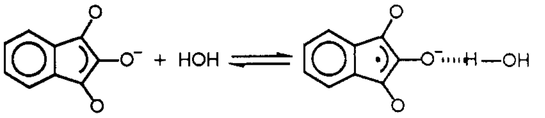
All of the anion radicals mentioned above will persist in the presence of water.[7] Consequently, the addition of ^{17}O-enriched water does not result in the immediate Birch reduction of the substrate. This, however, is not the case for many carbonyl-containing anion radicals, most importantly the ketyls. The addition of significant quantities of water to either the benzophenone or fluorenone ketyl results in the immediate loss of the ESR signal. Despite this, the addition of 1 μL of 20% $H_2{}^{17}O$ (0.05 mmol of water) to 10 mL of $\approx 10^{-2}$ M benzophenone or fluorenone anion radicals in HMPA results in the appearance of the ^{17}O-enriched ketyls. The only restriction is that the water cannot be in large molar excess relative to the amount of ketyl present. The water probably first protonates the ketyl in a disproportionation reaction producing ^{17}O-labeled hydroxide ion (A). This can then add to the neutral ketone resulting in the formation of the labeled ketone (B), which is consequently reduced via electron transfer (C), Scheme I.

Scheme I



The mechanism proposed in Scheme I is supported by the fact that hydroxide ion will react with anthraquinone ($C_{14}H_8O_2$) to form the hydroxide addition complex ($C_{14}H_8O_2$–OH^-).[8] Even in the systems where the anion radical persists in water, the anion radical acts as a strong enough base to deprotonate water, and the hydroxide addition must be followed by electron exchange. The indan-1,2,3-trione (ninhydrin) anion radical is a good example of such a system as it can be observed for hours after the addition of water up to the point where water accounts for 15% of the solvent.[9]

When water is added to a solution of the ninhydrin anion radical in HMPA, the anion radical persists, but the formation of hydrogen bonding between the water and the anion radical (reaction 3) results in a decrease in the larger proton coupling constants (A_H = 0.93 G, 2 H's, and A_H = 1.18 G, 2 H's), which is well documented.[9] However, when 5 μL of 20% $H_2{}^{17}O$ is added to 1.0 mL of a ca. 10^{-3} M



(3)

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[8] Roberts, J. L.; Sugimoto, H.; Barrette, W. C.; Sawer, D. T. *J. Am. Chem. Soc.* **1985**, *107*, 4556.

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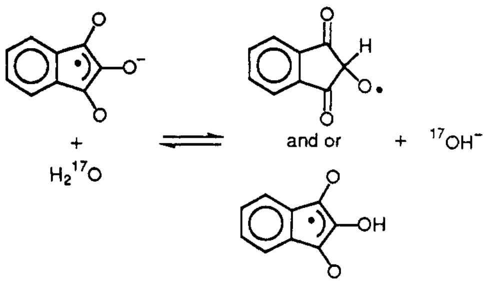
solution of the ninhydrin anion radical in HMPA, the expected changes in the coupling constants are accompanied by the nine-line spectrum being slowly replaced by that of the ^{17}O-substituted anion radical (A_0 = 3.94 G). The intensity of the ^{17}O-substituted system continues to grow for a period of about 30 h, and the two spectra can be observed simultaneously without apparent loss of total anion radical concentration. When the same reaction is carried out with a solution containing 0.1 M neutral triketone, the reaction is complete within 10 min. The anion radical solutions generated in the presence of excess neutral ninhydrin exhibit large line widths due to rapid electron exchange between neutral molecule and anion radical. The much more rapid appearance of the ^{17}O-labeled anion radical in the ESR spectra when the neutral molecule concentration in the anion radical solution is high, further supports the mechanism proposed in Scheme I and provides evidence against proton transfer from water to the anion radical to form hydroxide followed by direct reversible addition of hydroxide to the semiquinones and semidiones thereby exchanging oxygen. This dependance upon neutral molecule concentration also indicates that this same mechanism with the modification in step A indicated in reaction 4 is applicable for those systems that are kinetically stable in water. Once the labeled hydroxide ion is formed, the reaction can proceed in exactly the same manner as shown in Scheme I.



(4)

Several hours after the addition of large amounts (>10 μL) of labeled water, the ESR analysis clearly shows the presence of a third anion radical. This new system exhibits the same proton coupling constants and contains one ^{17}O with a much larger coupling constant (A_0 = 11.63 G). Given the relative slowness of the appearance of the second, larger ^{17}O splitting, it is statistically logical to assign this coupling constant to the unique carbonyl oxygen of the three. This is consistent with calculated Hückel and McLachlan type spin densities for the unique oxygen being more than double those of the matched pair of oxygens.[10] In our preliminary communication,[11] we misinterpreted the observation (at that time) of only one ^{17}O coupling constant in terms of the two oxygens being equivalent. This has proven not to be the case.

We were not able to observe a spectrum for any species containing two ^{17}O's on the same radical. This is due to statistical considerations coupled with the fact that the unlabeled material is always in much larger abundance than the labeled material. However, the reduction of specifically prepared dilabeled benzoquinone in liquid ammonia clearly shows the 11 five-line patterns due to four equivalent protons and two equivalent oxygen-17 nuclei.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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Synthesis of 1,1-Bishomoadamant-3-ene (Tricyclo[5.3.1.1^{3,9}]dodec-3-ene)

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Received April 3, 1989

Formation of the silyl enol ether of 1,1-bishomoadamantan-4-one (4) under thermodynamically controlled conditions gives 4-(trimethylsiloxy)-1,1-bishomoadamant-4-ene. Generation of the silyl enol ether of 4 under kinetically controlled conditions provides 4-(trimethylsiloxy)-1,1-bishomoadamant-3-ene. Consequently, 1,1-bishomoadamant-3-ene (3) can be prepared in two steps from 4 by Ireland's method for the conversion of a ketone to the corresponding olefin via the kinetic enolate. As predicted by the criteria of both Wiseman and Schleyer, 3 is a tricyclic bridgehead olefin that is kinetically stable at room temperature.

Since Bredt noted that double bonds tend to avoid the ring junctions in camphane and pinane systems,[1] the synthesis of bridgehead olefins has received considerable attention.[2] According to Wiseman's modification of Bredt's rule, the strain in *bicyclic* bridgehead alkenes can be related to the strain of *trans*-cycloalkenes.[3] Wiseman recognized that all isolable bicyclic bridgehead olefins possess a *trans*-cycloalkene moiety that has at least eight carbon atoms. Wiseman also predicted that bicyclic bridgehead olefins in which the *trans*-cycloalkene unit contains seven or less carbon atoms should not be observable at room temperature.

More recently, molecular mechanics calculations have been employed to predict the stability of bridgehead olefins.[4] The olefinic strain (OS) of an alkene is calculated by subtracting the total strain energy of the most stable conformer of the corresponding saturated hydrocarbon from the total strain energy of the most stable conformer of the olefin. For calculations performed with the MM1 force field, Maier and Schleyer concluded that if OS $\leq$ 17 kcal/mol, then the olefin will be "isolable" at room temperature. If 17 kcal/mol $\leq$ OS $\leq$ 21 kcal/mol, then the

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