CHEMISTRY LETTERS, pp. 637-640, 1988.

Spin-Trapped Alkyl Radicals in Dehydrogenation of Alkenes with 4-*t*-Butyl-*o*-benzoquinone

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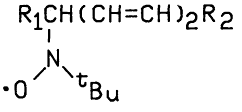
By the spin-trapping technique using 2-methyl-2-nitrosopropane as a spin trap conjugated hydrocarbon radicals have been detected in dehydrogenation of methyl linoleate and (2E,4E,7Z)-tetradecatriene with 4-*t*-butyl-*o*-benzoquinone.

Quinonoid compounds are efficient dehydrogenating agents, and dehydrogenation-addition occurs in reactions with some olefinic compounds.[1)] The mechanism of this reaction has been ascribed to either two-electron oxidation involving the transfer of a hydride in the rate determining step, or a one-electron oxidation with the hydrogen atom transfer. At the present, however, few reports described the detection of intermediate species which provide significant evidence to distinguish two possible mechanisms. Ansell and Bignold unsuccessfully applied the spin-trapping method to detect intermediate free radicals in the reaction of *o*-chloranil and tetramethylethylene, which yielded addition products.[2)]

Recently, it has been revealed that reactions of 4-*t*-butyl-*o*-benzoquinone (**1**) and several methylene-interrupted alkenes, i.e., methyl linoleate (**2**), 3-[(8'Z,11'E,13Z')-pentadecatrienyl]veratrole and 1,4-pentadiene (**3**), afford a series of isomers of 1:1-adduct through dehydrogenation-addition paths.[3] We have applied the spin-trapping technique to explore the initial stage of quinone dehydrogenation in these reactions, and report here that quinone 1 oxidizes olefin **2** and (2E,4E,7Z)-tetradecatriene (**4**) leading to the formation of hydrocarbon radicals which can be efficiently trapped by 2-methyl-2-nitrosopropane (NtB).

In Fig.1 are shown ESR spectra given at 1 h after mixing NtB (Aldrich), quinone **1**,[4] and olefins **4**[5] (A) or **2** (B) in benzene at 28 °C.[6] These ESR signal of the spin adducts appeared at several minutes after the mixing and the intensity gradually increased as the reaction proceeded with the six-line share of the spectrum unaltered for both reactions of **2** and **4**. Spectra A and B are essentially same and consist of a triplet of doublets with $a^N=1.49$ and $a^H=0.198$ mT; a small hyperfine splitting (ca. 0.03 mT) presumably due to β-protons was observed as well. This spectral feature is similar to that of the nitroxide spin adduct (**5**) given by autoxidation of **2** ($a^N=1.475$, and $a^H=0.175$ mT in tetrahydrofuran),[7] in which NtB links to C-9 or C-13. It has been reported that the reaction of NtB with unoxidized olefinic compounds did not give any radical adducts on incubation.[7] Further no spin adduct was detected in the oxidation of 4-*t*-butylcatechol with nickel peroxide in the presence of NtB. This seems reasonable since the expected semiquinone radical[8] may decay faster than semiquinone of hydroquinone which has the decay constant of ca. 10^9 $mol^{-1}dm^3s^{-1}$ (in H_2O),[9] and may not be trapped by NtB which captures a secondary alkyl radical with the rate constant of 6.1×10^6 $mol^{-1}dm^3s^{-1}$.[10] Therefore, the above ESR signals are concretely ascribed to spin adducts of alkyl radicals. It is likely that quinone **1** abstracts a hydrogen atom from the bisallylic position of olefins **4** (C-6) and **2** (C-11) followed by delocalization to give conjugated heptatrienyl and pentadienyl type radicals. The spin trap may predominantly attack either of the terminal positions of the conjugated moiety of these radicals which are of highest reactivities. This conforms to the fact that the hydrogen abstraction by radical initiators from other sites of **2** is much slower in autoxidation.[11]



$R_1CH(CH{=}CH)_2R_2$ with $N(\dot{O})({}^tBu)$ on the CH

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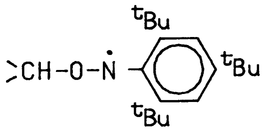

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On the other hand, the ESR spectrum given by the reaction of **3** was highly complicated as compared with spectra A and B, and greatly changed as the reaction proceeded. Fig.1c is the spectrum given at 1 h after mixing **1**, **3** and NtB. The sterically unhindered pentadienyl radical from **3** may be of high reactivity and easy to add to another molecule to yield various types of radical species.

The ESR signal of 2,4,6-tri-*t*-butylnitrosobenzene (BNB) spin adduct was also detected in the reaction of quinone **1** and olefin **2** in benzene. Although the spectrum was intricate, it was mainly composed of the signal with the hyperfine coupling constants a^N=0.96 and a^H=0.17 mT, which are close to those of the H-anilino type adduct (6) of secondary alkyl radicals (a^N=1.08, a^H=0.17 mT).[10,12] The formation of this type of adduct dominates in coupling of BNB with secondary alkyl radicals. Thereby, the production of hydrocarbon radicals in the dehydrogenation of **2** with quinone **1** has been confirmed.

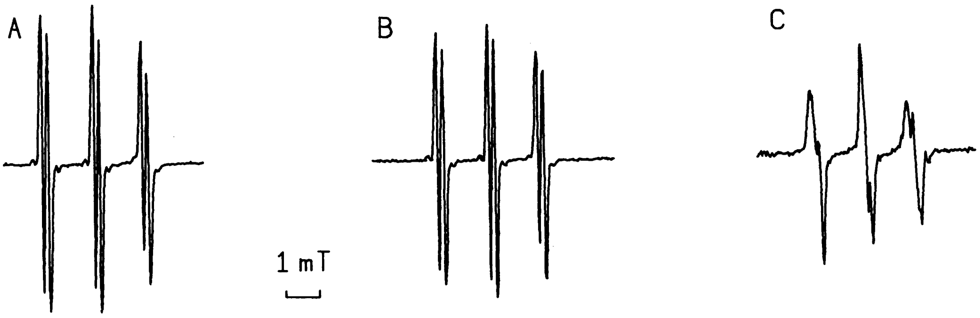

Fig. 1. ESR Spectra of NtB spin adducts derived by dehydrogenation of **4** (A), **2**, (B) and **3** (C) with quinone **1** in benzene.

The disappearance of quinone 1 by the reduction with **2** was followed at 380 nm, and revealed to be described by the first order kinetics with the rate constant of 5.3 x 10^{-5} $mol^{-1}dm^3s^{-1}$. This slow rate of the reduction is parallel with the slow emergence of the ESR signal of the spin trap. Actually, the number of spins generated after the 1 h's reaction (ca. 10^{18} cm^{-3}) was comparable to the values estimated from the above rate constant and concentrations of reagents (1 x 10^{18} cm^{-3}). The capturing rate constant of secondary alkyl radicals by NtB in benzene is sufficiently high as described earlier,[10] and any change in the shape of ESR signal of the NtB spin adduct was not apparent for at least several hours. Then it was inferred that almost all radicals produced in dehydrogenation of **2** and **4** were scavenged by NtB.

As a summary, it has been proved that α,ω-disubstituted hexatrienyl and pentadienyl radicals are derived at the initial step in quinone dehydrogenation of olefins **4** and **2** by the one-electron hydrogen atom transfer mechanism. This is, to our knowledge, the first direct observation of the hydrocarbon radicals formed in quinone dehydrogenation of olefins.

References

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5) Trien **4** was prepared by the partial hydrogenation on Lindlar catalyst of (2E, 4E)-tetradecatrien-7-yne which was obtained by coupling of the Grignard reagent from 1-octyne with 1-bromo-2,4-hexadiene (total yield, 85%); this structure was confirmed by GLC-MS (70 eV) and ^{1}H NMR (270 MHz) spectra.
6) ESR measurements were done on degassed benzene solutions (0.4 cm^3) of an olefin (0.2-0.3 mol dm^{-3}), quinone 1 (0.2 mol dm^{-3}) and a spin trap (5 mg) under vaccum with a JEOL FE-3X instrument. All the operations were done in the dark when NtB was used.
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(Received January 9, 1988)