concerning a possible role for Q_{10} in oxidative phosphorylation mechanisms; also, concerning analyses for vitamin E, since the chromanol II is a methoxy analog of vitamin E. However, the natural occurrence of the chromanol II has not yet been established.

CONTRIBUTION FROM THE
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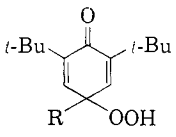
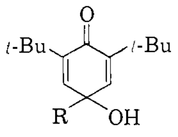
RECEIVED JULY 11, 1960

OXIDATION OF HINDERED PHENOLS TO SEMIQUINONES

Sir:

The reactions between oxygen and hindered phenols in alkaline solution have been reported in several recent papers.[1,2,3,4] The major products at low temperatures are peroxides of structure I which in alkaline solution can decompose[1,2] to II or III or rearrange to IV. Free radicals whose structure has not been explained heretofore have been observed[5,6] in this system by electron spin resonance (e.s.r.) spectroscopy.


I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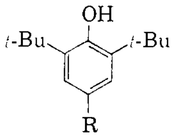
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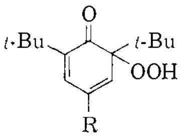
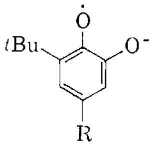

IV

We wish to report an unusual new reaction, isobutene elimination leading to the formation of pyrocatechol semiquinones V which are responsible for the observed e.s.r. spectra (Table I).


V

The isobutene evolved has been identified by gas-liquid chromatography and mass spectrometry. Two of the suspected pyrocatechols, 3-*tert*-butyl-5-methylpyrocatechol and 3,5-di-*tert*-butylpyrocatechol, have been prepared. The e.s.r. spectra of the semiquinones of these two compounds are identical with the spectra observed on oxidation 2,6-di-*tert*-butyl-4-methylphenol and 2,4,6-tri-*tert*-butylphenol, respectively.

TABLE I

PROPERTIES OF ELECTRON SPIN RESONANCE SPECTRA OF SEMIQUINONES OBTAINED BY OXIDATION OF 2,6-DI-TERT-BUTYL-4-R PHENOL

R	Approx. int. ratios of hyperfine lines	Coupling constants, gauss	
		a_1	a_2
Methyl	1:1:3:3:3:3:1:1	5.2	2.5
Benzyl[a]	1:1:2:2:1:1	4.1	2.5
Isopropyl[a]	1:2:1	2.4	2.4
tert-Butyl	1:1	..	2.5

[a] Provided by the courtesy of Dr. F. C. Davis and Dr. G. C. Coppinger of Shell Development Company.

If I (R = CH_3) is allowed to decompose in alkaline solution, the characteristic e.s.r. spectrum of the corresponding semiquinone appears in about four hours. If an equimolar solution of I and III (R = CH_3) or an equimolar solution of cumene hydroperoxide and II is made alkaline, a strong e.s.r. spectrum appears immediately. Gersmann and Bickel[2] have suggested that an orthoquinone formed by the decomposition of IV may be responsible for the autocatalytic behavior of the main oxidation reaction. The present work indicates that orthoquinones almost certainly are produced. The mechanism of the olefin elimination reaction giving rise to the orthosemiquinones and orthoquinones is obscure. It is probably significant that the product is an orthosemiquinone rather than a parasemiquinone even if R = *t*-butyl.

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[1] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).

[2] H. R. Gersmann and A. F. Bickel, *J. Chem. Soc.*, 2711 (1959).

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OPTICALLY ACTIVE VINYL POLYMERS. II. THE OPTICAL ACTIVITY OF ISOTACTIC AND BLOCK POLYMERS OF OPTICALLY ACTIVE α-OLEFINS IN DILUTE HYDROCARBON SOLUTION

Sir:

Although the existence of spiralized conformations of the macromolecules of many vinyl polymers in the solid state has been recognized since 1954,[1] no experimental evidence for the existence of such types of conformations in the liquid phase has been reported.

The data given here seem to support the hypothesis that, in the case of poly-α-olefins, helical conformations can exist above the melting point and in dilute solution.[2]

As we have reported recently,[3] the crystalline isotactic and block polymers of (+)(S)-3-methyl-1-

[1] G. Natta and co-workers, *Nuovo Cimento*, [X], Suppl. **15**, 1-158 (1960).

[2] G. Natta, *et al.* (private communication) have obtained some evidence for the existence of helical conformations of poly-α-olefins in solution from infrared spectra. Similar evidence has been obtained by H. Tadokoro, S. Nozakura, T. Kitazawa, Y. Yasuhura and S. Murahashi, (*Bull. Chem. Soc. Japan*, **31**, 313-315 (1958)).

[3] P. Pino, G. P. Lorenzi and L. Lardicci, abstracts of papers of Symposium for Macromolecular Chemistry, Moskow, 14-18, June, 1960. Communication to the Italian Chemical Society Meeting held in Florence on April 2nd, 1960, *Chimica e Industria*, **42**, in press (1960).