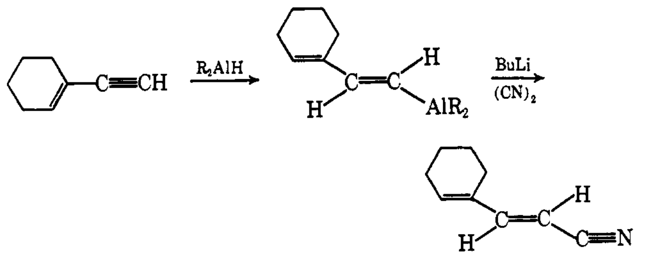

Finally, hydroalumination of phenylacetylene with diisobutylaluminum hydride at 50° affords 70% vinylalane and 30% alkynylalane.[7] Successive treatment of the reaction mixture with butyllithium and cyanogen gives, after fractional distillation, a 64% yield of *trans*-2-phenylethenenitrile.

The experimental results are summarized in Table I.

Since the nitrile group is readily converted into other functional groups (amides, amines, aldehydes, etc.), the present procedure provides a valuable tool for the preparation of numerous vinyl derivatives of defined stereochemistry. The simplicity of the procedure for the conversion of alkynes into *trans*-α,β-unsaturated nitriles is illustrated by the following example.

A dry 200-ml flask equipped with a side arm capped with a rubber septum, a thermometer well, and a magnetic stirrer was flushed with nitrogen. To the flask, which was kept under a static pressure of the gas, was added 4.1 g (50 mmol) of 1-hexyne, 20 ml of *n*-hexane, and 9.3 ml (50 mmol) of diisobutylaluminum hydride. The temperature during the addition was maintained at 25–30° by means of a water bath. The solution was stirred at room temperature for 30 min, then heated slowly to 50°. After remaining for 2 hr at this temperature, the reaction mixture was cooled to −20° (CCl_4–CO_2 bath) and 31 ml (50 mmol) of methyllithium in ether was added. Cyanogen (3 ml, 60 mmol) was condensed at −30° using a small cold trap.[8] The cooling bath was then removed and the cyanogen was allowed to pass into the vinylalanate solution while the temperature was maintained between −10 and +10°.[9] In order to avoid the escape of excess cyanogen, the reaction flask was connected to a wash bottle containing 6 *N* sodium hydroxide.[9] After addition of the cyanogen was completed the dark reaction mixture was stirred for an additional 30 min at room temperature before being poured into a well-stirred slurry of 3 *N* sodium hydroxide (100 ml) which had been precooled in a Dry Ice–acetone bath. The hydrolysate was allowed to come to room temperature and then was extracted with pentane. Distillation gave 4.7 g of *trans*-hept-2-enenitrile (87%); bp 112–114° (20 mm), n^{23}D 1.4397 (lit.[10] bp 186–187 (759 mm), n^{23}D 1.4399).

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[7] J. R. Surtess, *Australian J. Chem.*, **18**, 14 (1965).

[8] Cyanogen was obtained from the Matheson Co.

[9] In view of the fact that the reactions of cyanogen with vinylalanates or sodium hydroxide result in the formation of precipitates, the use of sintered-glass dispersion tubes should be avoided.

[10] P. Bruylants, *Bull. Soc. Chim. Belges*, **41**, 336 (1932).

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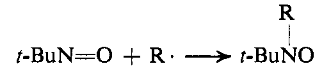
A Probe for Homolytic Reactions in Solution. II. The Polymerization of Styrene[1]

Sir:

There are now several examples in the literature of the observation by electron spin resonance of nitroxide radicals formed by the addition of reactive free radicals to C-nitroso compounds.[2] We wish to point out the potential value of this reaction as a probe for exploring the mechanisms of free-radical reactions in solution. This suggestion is based on the very large bimolecular rate constants estimated[3] for these additions, coupled with the exceptional stability of nitroxide radicals; consequently, sufficient nitroxide concentrations can readily be achieved for direct esr observation to be possible without recourse to flow-system techniques.

The nitroso compound of choice is 2-methyl-2-nitrosopropane (I), since nitroxides (II) derived from I exhibit hyperfine couplings due only to nitrogen and to the scavenged radical. Two disadvantages in the use of I are that unresolved coupling with the *t*-butyl protons gives rather broad lines and that red light is sufficient to effect photolysis of I (→ *t*-Bu· + NO),[4] and light must therefore be excluded during the preparation of samples.[5] Figure 1a shows a typical spectrum, obtained in this case by warming a dilute solution of lauryl peroxide and I in deoxygenated[6] benzene. Each of the nine principal lines, attributable to coupling with nitrogen plus two equivalent α-methylene protons (a_N = 15.0 G, a_H = 9.9 G), is further split into a partially resolved triplet, presumably by the β-methylene protons.



$$\underset{\text{I}}{t\text{-BuN=O}} + R\cdot \longrightarrow \underset{\text{II}}{t\text{-Bu}\overset{R}{\overset{|}{N}}O\cdot}$$

Application to a more complex reaction is illustrated in Figures 1b–e, which show spectra of radicals generated during the polymerization of styrene initiated by *t*-butyl peroxyoxalate (*ca.* 15 mg of peroxyoxalate/ml of styrene) at room temperature in the presence of I. The highest concentrations of I (*ca.* 0.05 *M*) gave the spectra shown in Figures 1b,c. In Figure 1b the two outermost lines are part of the known three-line spectrum of *t*-BuO(*t*-Bu)NO·[7] which results from scavenging of the

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[1] G. R. Chalfont and M. J. Perkins, *J. Am. Chem. Soc.*, **89**, 3054 (1967), is regarded as part I of this series.

[2] For recent examples see ref 1 and A. Mackor, T. A. J. W. Wajer, and T. J. de Boer, *Tetrahedron*, **24**, 1623 (1968).

[3] For example, the "methyl affinity" of nitrosobenzene at 65° is greater than that of benzene by *ca.* 10^5: W. J. Heilman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1127 (1957); the rate constant for reaction of $\cdot CH_3$ with benzene has been estimated at 50 l. mol^{-1} sec^{-1} at 80°: D. F. DeTar, *J. Am. Chem. Soc.*, **89**, 4058 (1967); these figures put the rate of reaction of $\cdot CH_3$ with C_6H_5NO within 2–3 orders of magnitude of the diffusion-controlled limit. (It is, however, not certain that all of this reaction occurs at nitrogen.)

[4] A. Mackor, T. A. J. W. Wajer, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 2115 (1967); J. G. Calvert and S. S. Thomas, unpublished work quoted in J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 476.

[5] The *t*-butyl radicals are readily scavenged to give di-*t*-butyl nitroxide,[3] the spectrum of which may mask that of radicals under investigation. In some instances, on the other hand, this photolysis may constitute a useful radical initiation.

[6] A solution of lauryl peroxide (*ca* 0.4 ml, 5%) was added to the solid nitroso dimer (*ca* 0.1 mg) in a quartz esr tube, and the solution was deoxygenated by a stream of oxygen-free nitrogen. The tube was capped to exclude air and heated in the cavity of the spectrometer. All samples were similarly deoxygenated before spectroscopic examination.

[7] A. Mackor, T. A. J. W. Wajer, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 385 (1967).

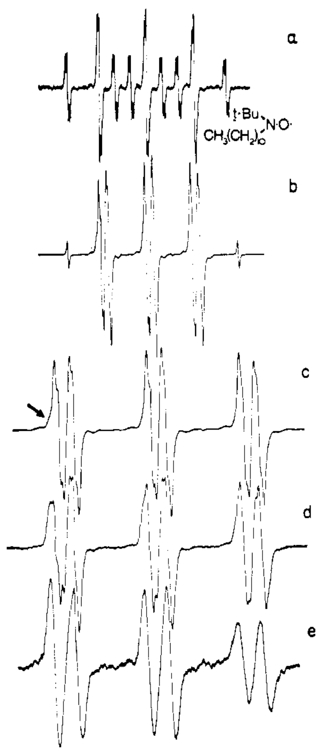
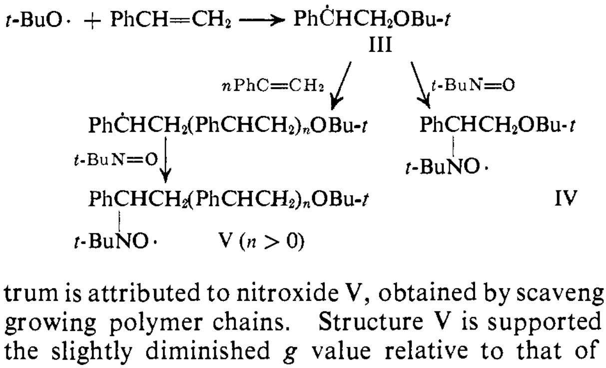


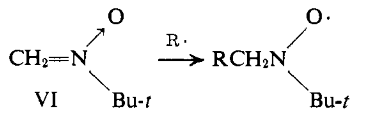
Figure 1. Esr spectra of nitroxides RN(t-Bu)O·; for details, see text.

initiating butoxy radical. The remainder of the spectrum (expanded in Figure 1c) is principally attributed to the nitroxide IV which arises by scavenging of the first-formed carbon radical III and has $a_N = 14.3$ G, $a_H = 2.3$ G.[8] In a series of separate experiments in which the scavenger concentration was gradually reduced, the relative intensity of the shoulder (arrow in Figure 1c), increased (see Figure 1d) until a new six-line spectrum (Figure 1e; $a_N = 14.5$ G, $a_H = 3.3$ G; scavenger concentration *ca.* 0.001 M) was observed in which no β splittings could be resolved. The new spectrum is attributed to nitroxide V, obtained by scavenging growing polymer chains. Structure V is supported by the slightly diminished g value relative to that of IV (consistent with the more remote placement of butoxy oxygen) as well as by the pronounced line-width variations.



Preliminary results have also been obtained with other monomers and initiators. These experiments are very easily carried out, and in this respect they compare favorably with the elegant flow-system studies of polymerization described by Fischer.[9]

Very recently a somewhat similar trapping technique utilizing t-butyl phenyl nitrone has been reported.[10] In related experiments we have found that the methylene nitrone VI prepared by the procedure recently described by Baldwin, *et al.*,[11] is particularly effective in this respect. Details of this aspect of the work will be presented in the full paper.



Acknowledgment. We are grateful to Varian Associates Ltd. for a summer visitorship (to M. J. P.) and to the Science Research Council for a studentship (to G. R. C.).

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[8] The magnitude of the α-hydrogen couplings varies markedly with the bulk (and conformational effects) of other substituents: M. McMillan and R. O. C. Norman, *J. Chem. Soc., B*, 590 (1968).

[9] H. Fischer, *Z. Naturforsch.*, **19a**, 866 (1964).

[10] E. G. Janzen and B. J. Blackburn, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. ORGN-86. We are grateful to one of the referees for bringing this abstract to our attention. The formation of nitroxides by addition of radicals to nitrones has also been recorded by M. Iwamura and N. Inamoto, *Bull. Chem. Soc. Japan*, **40**, 702 (1967).

[11] J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *Chem. Commun.*, 373 (1968); J. E. Baldwin, R. G. Pudussery, A. K. Quereshi, and B. Sklarz, *J. Am. Chem. Soc.*, **90**, 5325 (1968).

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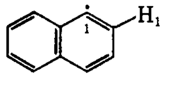
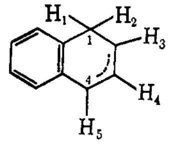
Electron Paramagnetic Resonance Study of Free-Radical Reactions Initiated by Radioactive Decay in Solid Naphthalene-1-*t*

Sir:

We wish to report the production of free radicals in pure, solid naphthalene by the radioactive decay of tritium specifically substituted into the naphthalene molecule. In comparison, free radicals are *not produced* in solid naphthalene by X-irradiation.[1] Two radical species were found, one previously unknown. The first, which appeared soon after the preparation of the sample and which was stable at liquid nitrogen temperature, is tentatively identified as 1-naphthyl (I). Radical II, which is stable at room temperature, is identified as 1-hydronaphthyl.



I



II

Two samples of naphthalene enriched with naphthalene-1-t were prepared, one in single-crystal form and one in polycrystalline form. For the single crystal, carrier-free naphthalene-1-t was prepared by the Grignard reaction from 1-bromonaphthalene and 3 Ci (2.4 STP cc) of carrier-free tritium chloride (TCl), which in turn was made by sparking stoichiometric quantities of tritium and chlorine gases. The tritiated naph-

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[1] D. E. Wood, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1964.