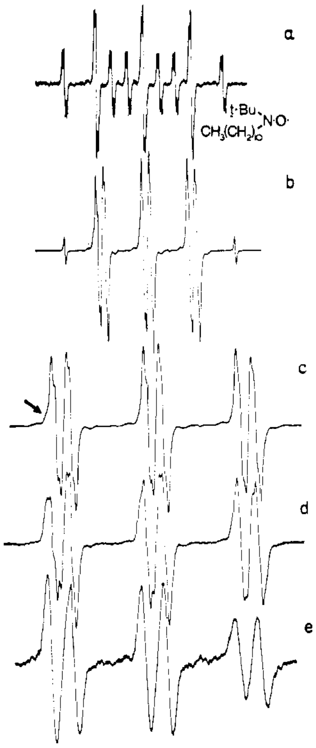
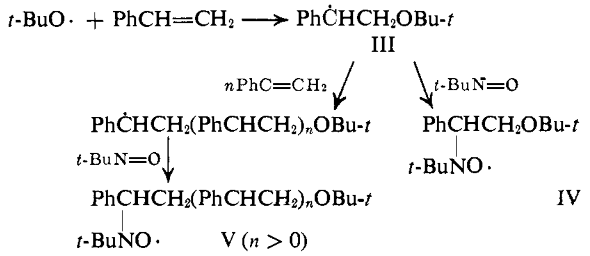


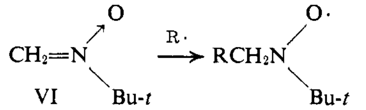
Figure 1. Esr spectra of nitroxides RN(*t*-Bu)O·; for details, see text.

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.



VI

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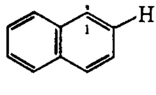
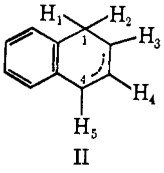
Electron Paramagnetic Resonance Study of Free-Radical Reactions Initiated by Radioactive Decay in Solid Naphthalene-1-*t*

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.

thalene thus prepared (theoretical yield 14 mg) was added to 1 g of degassed, zone-refined naphthalene, and a single crystal was grown in a sealed quartz tube by the Bridgeman method. The polycrystalline sample was prepared by adding sufficient anhydrous HCl to the carrier-free tritium chloride to yield 1 g of naphthalene from the Grignard reagent. All manipulations were carried out in a vacuum line in the strict absence of oxygen. The following materials were used without further purification: 1-bromonaphthalene, Eastman Grade, Eastman Organic Chemicals; ethyl ether, Anhydrous AR, Mallinckrodt; magnesium turnings, Grignard Grade, Fisher; tritium gas, Carrier Free, New England Nuclear Corp.; Cl_2, High Purity Grade, and HCl, Electronic Grade, Air Products and Chemicals Inc. Baker Analyzed Reagent Grade naphthalene was further purified by ten passes through a 20-mm diameter zone refiner.[1]

The epr spectrometer used was essentially a Varian Associates 100-kHz field modulation, homodyne spectrometer operating at 9.1 GHz with a second field modulation at 400 Hz for second derivative presentation. The epr cavity was designed such that any orientation of the sample with respect to the external magnetic field could be obtained *via* rotation of the goniometer holding the sealed sample tube or rotation of the magnet. In this manner it was not necessary to remove the sample from its tube for the epr measurements.

The polycrystalline sample, when run at 77°K soon after its preparation, gave a spectrum consisting simply of two broad lines with a separation of 17 G. We tentatively identify the radical species responsible as 1-naphthyl (I), with the two-line spectrum arising from the interaction of the unpaired electron with proton 1. An INDO calculation[2] gives an isotropic splitting of 17.9 G for proton 1 and also indicates that the radical should be a σ type. Three other positions in the radical should have isotropic splittings of about 5 G which together with the other smaller splittings would be expected to broaden the epr spectrum to the point that only the 17.9-G splitting could be resolved. When the polycrystalline sample was examined at 77°K after having been stored at 77°K for 154 days, the spectrum showed a small amount of contamination from 1-hydronaphthyl (see below) superimposed on top of the 1-naphthyl spectrum. Upon being warmed to room temperature the sample immediately gave the nine-line spectrum in Figure 1C. This corresponds closely to the spectrum found by Leone and Koski[3] for irradiated naphthalene in methanol at 77°K and identified by them as arising from 1-hydronaphthyl (referred to in their paper simply as naphthyl). The spectrum is a triplet of triplets with major and minor splittings of 34.6 and 13.1 G, respectively. Leone and Koski found 37 and 12.8 G. The g value is 2.0030 ± 0.0002; by comparison with DPPH, $g = 2.0036$. The large splitting is from the equivalent β protons 1 and 2, and the smaller splitting is from the almost equivalent allylic protons 3 and 5. It should be remarked at this point that the intensity of the 1-hydronaphthyl spectrum in Figure 1C is approximately the same as the total intensity of the 1-naphthyl and 1-hydronaphthyl just prior to warming the sample to room temperature. That is, the 1-naphthyl radical seems to produce a like amount of 1-hydronaphthyl radical upon being warmed to room temperature.

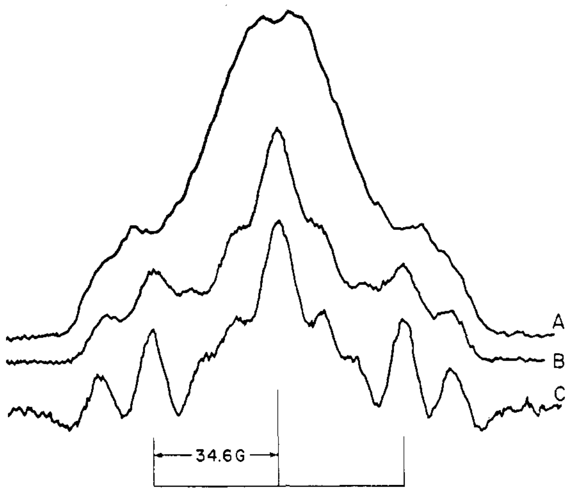

Figure 1. Second-derivative epr spectra of naphthalene-1-*t* at room temperature: (A) single-crystal sample with magnetic field perpendicular to *ab* plane; (B) single-crystal sample with magnetic field in *ab* plane; (C) polycrystalline sample.

The single-crystal sample observed at room temperature gave spectra of six, nine, or twelve lines depending on the orientation of the sample with respect to the external magnetic field. An example of the nine-line spectrum is shown in Figure 1B, taken with the magnetic field in the crystal *ab* plane. An INDO calculation gives isotropic hyperfine coupling constants of -12.1, $+5.4$, and -11.3 G for protons 3, 4, and 5, respectively, and p-orbital spin densities of $+0.4813$, -0.2337, and $+0.4663$ for carbon atoms 2, 3, and 4, respectively.[2] Using these values together with the dipolar hyperfine tensors for malonic acid radical, we calculate the principal values of the hyperfine tensors to be (-17.4, -12.2, -6.8), ($+8.0$, $+5.5$, $+2.8$), and (-16.4, -11.4, -6.1) for protons 3, 4, and 5, respectively.[4] The experimentally observed maximum of 21.7 G and minimum of 7.1 G for the allylic protons should be compared to the calculated values of -17.4 and -6.1 G. The splitting from the middle allylic proton, 4, is not resolved at any orientation. Using the above calculated values of the hyperfine tensors to obtain a theoretical epr spectrum at a magnetic field orientation perpendicular to the *ab* plane, we obtain -7.31, $+6.1$, and -14.94 G for protons 3, 4, and 5, respectively. Figure 1A shows the spectrum taken with this magnetic field orientation, where all the naphthalene sites in the unit cell will be magnetically equivalent, and thus also 1-hydronaphthyl radicals in naphthalene sites.[5] This spectrum is interpreted as showing, in addition to the β-proton splittings of 34.6 G, a splitting of about 12 G and a very poorly resolved splitting of about 6 G. It is readily appreciated that any splitting less than 6 G would not be resolved at this orientation. This resolution was, unfortunately, not improved by lowering the temperature to 77°K.

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(2) P. A. Dobosh, Carnegie-Mellon University, personal communication, 1968.

(3) J. A. Leone and W. A. Koski, *J. Am. Chem. Soc.*, **88**, 656 (1966).

(4) H. M. McConnell, H. C. Heller, T. Cole, and R. W. Fessenden, *ibid.*, **82**, 766 (1960).

(5) J. M. Robertson, *Acta Cryst.*, **2**, 238 (1949).

The following reaction scheme accounts for the previously mentioned formation of 1-hydronaphthyl from 1-naphthyl and for the fact that radicals were not observed in irradiated naphthalene which received the same dosage from X-rays as the samples enriched in naphthalene-1-*t* received from tritium β radiation (60–90 Mrads).

$$\mathrm{RT} \longrightarrow \mathrm{RHe}^+ + \beta^- \tag{1}$$

$$\mathrm{RHe}^+ \longrightarrow \mathrm{R}^+ + {}^3\mathrm{He} \tag{2}$$

$$\mathrm{R}^+ + \mathrm{e}^- \longrightarrow \mathrm{R}\cdot\ (\mathrm{I}) \tag{3}$$

$$\mathrm{R}\cdot + \mathrm{RH} \longrightarrow \mathrm{RR} + \mathrm{H}\cdot \tag{4}$$

$$\mathrm{H}\cdot + \mathrm{RH} \longrightarrow \mathrm{RH}_2\cdot\ (\mathrm{II}) \tag{5}$$

Reaction 1 is the spontaneous radioactive decay of tritium with a half-life of 12.26 years and a maximum β particle energy of 18.1 keV. The maximum recoil energy of 3.3 eV for the ^{3}He ensures that the species formed in reaction 1 will not have its nuclear framework destroyed by the primary event. The order of, or even the separate existence of, reactions 2 and 3 are of course uncertain; however, the neutralization of ionic species would be expected in the semiconducting lattice of naphthalene. Reaction 4 can occur between neighboring naphthalene sites with relatively little displacement from the equilibrium positions. The coupling would be between positions 1 on one naphthalene and 2 on the other. The existence of reaction 5 was demonstrated by Leone and Koski in frozen alcohol solutions.[3]

We seem to have here a unique system which offers the opportunity to study free-radical reactions upon which certain geometrical constraints can be placed. Further experiments are being planned to check the hypotheses put forward in this communication and, if possible, to obtain rate constants and activation energies for the reactions occurring in the solid state.

Acknowledgment. This work was aided by a National Science Foundation instrument grant.

[6] Recipient of a grant from the Minnesota Mining and Manufacturing Co.

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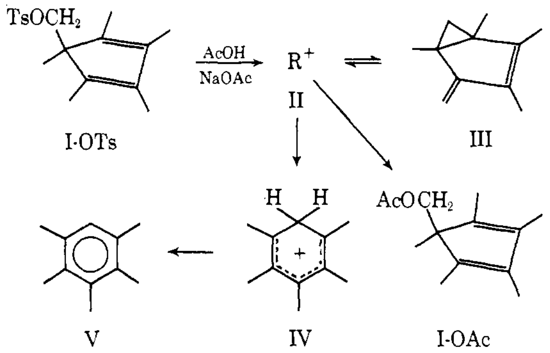
Received October 14, 1968

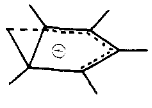
The Observation and Behavior of the Pentamethylcyclopentadienylmethyl Cation[1,2]

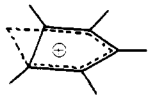
Sir:

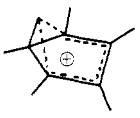
In this communication we return to the subject of the intermediate nonclassical ion or ions (II) in the solvolysis of pentamethylcyclopentadienylmethyl *p*-toluenesulfonate (I-OTs).[3] As reported some years ago,[3] acetolysis of this system is tremendously anchimerically accelerated, the product of kinetic control being nearly entirely olefin III with a very small proportion of acetate I-OAc. On standing in acetic acid solution, even under basic conditions (0.11 *M* NaOAc), olefin III adds acetic acid, and I-OAc becomes the major component of the III–I-OAc mixture. Under such conditions pentamethylbenzene (V) was not observed, no leakage from II to the pentamethylbenzenonium ion IV being detectable. Under more vigorous acidic conditions, permitting many repeated regenerations of II, pentamethylbenzene became a minor, or even a major, product.

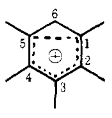


While it was clear from the former work that II was nonclassical,[3] it was not entirely clear how to represent the electron delocalization nor how many such discrete species need be written. This was illustrated[3a] with ions IIa, termed homoallylic, IIc, called doubly homoallylic,[3c] and IId, monohomocyclopentadienyl.


IIa


IIb


IIc



IId

We have now been able to observe ion II directly by nmr in FSO$_3$H medium and to study the thermal conversion of II to IV, as well as the photochemical transformation of IV to II. The results are outlined and discussed in the present communication.

Extraction of olefin III from methylene chloride or preferably chloroform into FSO$_3$H at low temperature[4] gives a good yield of a cation whose nmr spectrum is clearly consistent with the bicyclo[3.1.0]hexenyl structure[5] II (leaving aside the question of the degree or mode of cyclopropane involvement). In the nmr spectrum[7] the methyl group singlets appear at τ 8.34 (2 CH$_3$), 7.42 (2 CH$_3$), and 8.17 (1 CH$_3$), and the cyclopropane methylene proton doublets appear at τ 7.55 and 6.63. The latter are absent in the spectrum of the cation from protonation of the dideuterioolefin III-D. As regards electronic structure of ion II, it is impressive that the cyclopropane methylene protons are deshielded

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[1] Research supported in part by the National Science Foundation and in part by the U. S. Army Research Office.

[2] Reported at the 12th Reaction Mechanisms Conference, Brandeis University, June 19–22, 1968.

[3] (a) S. Winstein and M. Battiste, *J. Am. Chem. Soc.*, **82**, 5244 (1960); (b) L. de Vries, *ibid.*, **82**, 5242 (1960); (c) for structure IIc we had visualized[3a] overlap between one lobe of a p or hybrid orbital on the CH$_2$ carbon atom with each of the p orbitals on the terminal carbon atoms of the butadiene system. See the following communication for a different orbital arrangement in the transition state for the degenerate "cyclopropane merry-go-round."

[4] Attempted conversion of carbinol I-OH to II in FSO$_3$H or FSO$_3$H–SbF$_5$–SO$_2$ was unsuccessful, giving large amounts of polymer and a complex unrecognizable nmr spectrum.

[5] The bicyclo[3.1.0]hexenyl cation seems to be a possible intermediate in many recently described reactions. Some of the products from the reaction of benzvalene and substituted benzvalenes[6a] in acidic or protic media could involve this cation. This is true also of the photochemical transformation[6b] of benzene in acidic media, although the exact timing of the protonation is not clear.[6c]

[6] (a) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **88**, 2881 (1966); **89**, 1031 (1967); (b) E. Farenhorst and A. F. Bickel, *Tetrahedron Letters*, 5911 (1966); (c) D. Bryce-Smith, A. Gilbert, and H. C. Longuet-Higgins, *Chem. Commun.*, 240 (1967).

[7] All chemical shifts for the cations are referred to internal CH$_2$Cl$_2$ taken as τ 4.70.