In contrast, the kinetic energy release distributions for the loss of CO from furan and the two pyrones show that a wide range of kinetic energies is released upon fragmentation. This implies that considerable excess energy is required for these $[C_4H_4O]^{+\cdot}$ ions to rearrange to the transition state for the dissociation step. Indeed, the loss of CO from $[\text{furan}]^{+\cdot}$ has such a high activation energy[21] that the energy level of the transition state (~280 kcal mol^{-1}) makes thermochemically feasible the participation of many isomeric $[C_4H_4O]^{+\cdot}$ structures (cf. Table I).

Therefore, for these isomeric $[C_4H_4O]^{+\cdot}$ ions no firm deductions can be made from metastable peak characteristics concerning the structures of either the reacting or the nonreacting ions. Pirkle and Dine's deuterium labeling experiments[3] elegantly demonstrate that the metastably fragmenting (but energy rich) $[C_4H_4O]^{+\cdot}$ ions from 2-pyrone do not undergo reversible ring closure. However, this conclusion may not be extrapolated to the structure of the ions which give rise to the intense peaks at m/z 68 in the normal 70-eV mass spectra of both pyrones. These peaks largely consist of $[\text{furan}]^{+\cdot}$ ions.

Experimental Section

The collisional activation and the metastable ion (MI) spectra were measured on a Vacuum Generators ZAB-2F double-focussing mass spectrometer of reversed Nier-Johnson geometry. A 100-μA ionizing electron beam of 70 eV and an accelerating potential of 7920 V were used; sample reservoir and ion source temperatures were ~130 °C. The magnetic field was set to select the m/z 68 $[C_4H_4O]^{+\cdot}$ precursor ions; ionic products of their metastable decompositions (the MI spectrum) occurring in the field free drift region between the magnetic and electrostatic analyzers were measured by scanning the electrostatic analyzer (ESA) potential under conditions of good energy resolution. (Main beam width was 0.10 V at an ESA voltage of 422.1 V.) Kinetic energy releases were calculated in the usual way and corrected for limiting half-height width of the main beam. CA spectra were obtained in the same way after introduction of helium as a collision gas in the collision chamber near the β focal point. An external voltage (−320 V) was applied on the chamber to separate the normal metastable peaks from the CA peaks.

Acknowledgment. We thank Dr. F. P. Lossing for measurements of ionization and appearance energies and Dr. W. H. Pirkle for a gift of 2-pyrone. J. L. Holmes thanks the National Research Council of Canada for continuing financial support.

References and Notes

(1) (a) University of Ottawa; (b) University of Utrecht.
(2) (a) J. L. Holmes, *Int. Rev. Sci., Phys. Chem. Ser. Two*, **5**, 241 (1975); (b) F. W. McLafferty and W. T. Pike, *J. Am. Chem. Soc.*, **89**, 5954 (1967).
(3) W. H. Pirkle and M. Dines, *J. Am. Chem. Soc.*, **90**, 2318 (1968).
(4) F. P. Lossing and J. C. Traeger, *Int. J. Mass Spectrom. Ion Phys.*, **19**, **9** (1976).
(5) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
(6) J. L. Holmes, A. D. Osborne and G. M. Weese, *Int. J. Mass Spectrom. Ion Phys.*, **19**, 207 (1976).
(7) J. L. Holmes and A. D. Osborne, *Int. J. Mass Spectrom. Ion Phys.*, in press.
(8) These E_{rev} values are almost certainly *too low;* the calculation assumes that *all* of E_{rev} is measured from T_{min}, i.e., that all of E_{rev} is partitioned into translational degrees of freedom.
(9) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, **6**, (1977).
(10) J. L. Holmes, J. K. Terlouw, and F. P. Lossing, *J. Phys. Chem.*, **80**, 2860 (1976).
(11) J. L. Holmes, J. K. Terlouw, P. C. Vijfhuizen, and C. A'Campo, *Org. Mass Spectrom.*, **14**, 204 (1979).
(12) J. K. Terlouw, P. C. Burgers and J. L. Holmes, *J. Am. Chem. Soc.*, **101**, 225 (1979).
(13) K. Levsen and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, **15**, 509 (1976).
(14) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 244 (1973).
(15) R. G. S. Pong and J. S. Shirk, *J. Am. Chem. Soc.*, **95**, 248 (1973).
(16) A. Krantz, *J. Am. Chem. Soc.*, **96**, 4992 (1974).
(17) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Am. Chem. Soc.*, **91**, 1875 (1969).
(18) T. W. Bentley, *Spec. Period. Rep.: Mass Spectrom., Chem. Soc. London*, **4** (1977).
(19) P. Brown and M. M. Green, *J. Org. Chem.*, **32**, 1681 (1967).
(20) J. L. Holmes and A. D. Osborne, *Int. J. Mass Spectrom. Ion Phys.*, **23**, 189 (1977).
(21) AE ($[C_3H_4]^{+\cdot}$) from furan = 11.80 eV, measured with energy selected electrons.[4] Note that this energy lies above the calculated thermochemical thresholds for production of CO ($\Delta H_f = -26.4$ kcal mol^{-1})[9] and AE($[CH_2{=}C{=}CH_2]^{+\cdot}$) = 10.88[9] or $[CH_3C{\equiv}CH]^{+\cdot}$ = 11.48 eV[9]—and even AE($[\text{cyclopropene}]^{+\cdot}$) = 11.74 eV.[9] The discontinuity in the energy release distribution (Figure 1) may reflect the co-generation of two different product ion structures. The large activation energy may represent that required for ring opening.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 34. Rate Constants for Spin Trapping. 2. Secondary Alkyl Radicals[1]

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Abstract: The cyclization of the secondary 6-hepten-2-yl radical to form the primary 2-methylcyclopentylcarbinyl radical has been studied by kinetic EPR spectroscopy. The rate constant for this cyclization, k_c, can be represented by $\log (k_c/\text{s}^{-1}) = (9.8 \pm 0.3) - (6.4 \pm 0.3)/\theta$ where $\theta = 2.303RT$ kcal/mol. This cyclization has been used as a standard to measure the absolute rate constants for the spin trapping of secondary alkyls in benzene at 40 °C by a few of the more commonly employed spin traps. These results are compared with the previously determined[4] k^T values for trapping primary alkyl radicals under the same conditions. Relative k^T values for trapping of the tertiary 2-phenylprop-2-yl radical have also been measured.

Spin trapping[3] is an EPR spectroscopic technique that has proved immensely valuable in studies of reaction mechanisms because it allows transient radicals, R·, to be "visualized" by reacting them with a spin trap, T, to form a persistent spin adduct, RT·:

$$R\cdot + T \xrightarrow{k^T} RT\cdot$$

As we have pointed out previously,[4] spin trapping will only achieve its full potential when quantitative data on the rate constants, k^T, for trapping of all types of R· radicals become available. In our initial studies of spin-trapping rates[4,5] we worked with primary alkyl radicals. In the present paper, we report an extension of this work to secondary alkyls. Our experimental procedure is almost unchanged. In the earlier

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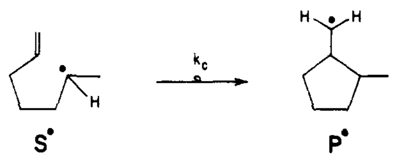
work[4,5] we relied primarily on the cyclization of the 5-hexenyl radical and distinguished between the spin adducts of the unrearranged and rearranged primary alkyls by means of ^{13}C labeling. In the present work we have relied primarily on the cyclization of the *secondary* 6-hepten-2-yl radical, S·, to form the *primary* 2-methylcyclopentylcarbinyl radical, P·. In the present case, there is no need to distinguish the unrearranged and rearranged radicals by isotopic labeling since these radicals are self-labeled by having one or two hydrogens, respectively, at their radical centers. This rearrangement is known to be irreversible[6] and to occur at a rate that is slightly faster than the 5-hexenyl cyclization.[6,7] In the presence of a trap two spin adducts will be formed:



$$S\cdot + T \xrightarrow{k^T} ST\cdot$$

$$P\cdot + T \rightarrow PT\cdot$$

The rate constant for spin trapping is given by[4]

$$k^T = \frac{k_c(\mathrm{d}[ST\cdot]/\mathrm{d}t)_{t\to 0}}{[T](\mathrm{d}[PT\cdot]/\mathrm{d}t)_{t\to 0}} \qquad (1)$$

In deriving this equation it is assumed that all of the alkyl radicals formed are captured by the trap.[4] This means that the rate of all other processes which lead to their consumption must be much less than the rate of trapping. In the *early* stages of the reaction only bimolecular reactions between alkyl radicals (rate constants ca. 10^9 M^{-1} s^{-1})[8] might be able to compete with trapping.[9] An "effective" trap will therefore be one for which $k^T[T]([S\cdot] + [P\cdot]) \gg 10^9([S\cdot] + [P\cdot])^2$ and since trap concentrations can hardly be greater than 1 M this means that $k^T \gg 10^9([S\cdot] + [P\cdot])$. The limit set by this condition depends on the rate, v_i, at which alkyl radicals are produced. Quantitative spin trapping experiments are most easily done with very low rates of radical formation, i.e., with $v_i \sim 10^{-8}$–10^{-9} M s^{-1}. This puts an effective lower limit on k^T of ca. 10^2 M^{-1} s^{-1}, though a trap with such a low k^T value would be very inefficient. It is, perhaps, also worth pointing out that if a rearrangement is to compete with spin trapping then $k_c \sim k^T[T]$. Therefore rearrangements that have unimolecular rate constants of ca. 10^2 s^{-1} can only be used to measure spin trapping rate constants with very inefficient traps. More efficient traps require faster rearrangements.

Experimental Section

Materials. Diacyl Peroxides. Di(2-methyl-6-heptenoyl) peroxide (**1**) was prepared starting with 5-bromo-1-pentene and diethyl methylmalonate. Dry ethanol[10] (57 mL) was refluxed for 2 h over 3.9 g of clean sodium cut into small pieces. After cooling, diethyl methylmalonate (29.6 g, 0.17 mol) was added, followed by 5-bromo-1-pentene (25 g, 0.168 mol). This mixture was refluxed for 3 h and cooled, and 200 mL of H_2O was added. Extraction with ether followed by distillation yielded 37 g of crude **diethyl 4-pentenylmethylmalonate** (yield 90%). This was purified by preparative VPC (10 ft 20% O.V. 101 column at 180 °C) to remove small amounts of impurities (chiefly diethyl 4-pentenylmalonate) and 22.3 g of extremely pure (>99.9%) diethyl 4-pentenylmethylmalonate was recovered. ^1H NMR ($CDCl_3$, δ values downfield from Me_4Si): 1.1–2.3 (t + m, 15 H, CH_3 and CCH_2C), 4.2 (q, 4 H, OCH_2), 4.9–5.2 (m, 2 H, $H_2C{=}C$), 5.5–6.2 (m, 1 H, C=CH).

This malonic ester (21.8 g, 0.09 mol) was hydrolyzed by heating for 12 h at 120 °C with 30 g of KOH in 100 mL of water.[11] The aqueous phase was acidified (2 N HCl) and extracted with ether, the extract was dried, and, on removal of the solvent, 15.8 g of solid **4-pentenylmethylmalonic acid** was obtained (yield 94%), mp 83.2 °C. ^1H NMR ($CDCl_3$): δ 1.1–2.3 (s + m, 9 H, CH_3 and CCH_2C), 4.9–5.2 (m, 2 H, $H_2C{=}C$), 5.5–6.2 (m, 1 H, C=CH), 12.0 (s, 2 H, OH).

The malonic acid (15 g) was heated to 250 °C and the decarboxylated **2-methyl-6-heptenoic acid** (bp 243 °C) was distilled off continuously. ^1H NMR ($CDCl_3$): δ 1.1–1.2 (d, 3 H, CH_3), 1.3–2.8 (m, 7 H, CH and CCH_2C), 4.9–5.2 (m, 2 H, $H_2C{=}C$), 5.5–6.2 (m, 1 H, C=CH), 12.1 (s, 1 H, OH).

The 2-methyl-6-heptenoic acid was converted to **di(2-methyl-6-heptenoyl) peroxide** (**1**) by the carbonyldiimidazole method.[4,12] ^1H NMR ($CDCl_3$): δ 1.1–1.2 (d, 3 H, CH_3), 1.3–2.8 (m, 7 H, CH and CCH_2C), 4.9–5.2 (m, 2 H, $H_2C{=}C$), 5.5–6.2 (m, 1 H, C=CH). Titration:[13] 86 ± 1% peroxide.

Di(2-methyl-6-heptanoyl) peroxide (**2**) was prepared by a similar procedure starting with 1-bromopentane. ^1H NMR ($CDCl_3$): δ 0.9–1.9 (d, m, 28 H, CH_3, CCH_2C), 2.1–2.6 (m, 2 H, CH). Titration:[13] 92 ± 2% peroxide.

2-Bromo-6-heptene (**3**) was prepared starting with 5-bromo-1-pentene (25 g) which was converted (with 4.3 g of Mg in 125 mL of ether) to the Grignard and this was treated with 12.3 g of freshly distilled acetaldehyde. Conventional workup followed by distillation gave 10.8 g of pure 6-hepten-2-ol (yield 59%). Reaction of this alcohol with PBr_3 according to the method of Johnson and Owyang[14] gave, after distillation, 2.8 g of **2-bromo-6-heptene** (yield 28%, purity 96%), bp 72 °C at 20 Torr. After preparative VPC (10 ft, 10% O.V. 101 column at 130 °C) 1.2 g of 99.8% pure bromide was recovered. ^1H NMR ($CDCl_3$): δ 1.5–2.2 (d, m, 9 H, CH_3 and CCH_2C), 4.0–4.4 (sextet, 1 H, CH), 4.8–5.1 (m, 2 H, $H_2C{=}C$), 5.4–6.2 (m, 1 H, C=CH).

Spin Traps. The following spin traps were either available from our earlier work[4] or were prepared by the same methods:[4] **2-methyl-2-nitrosopropane** (**NtB**), **nitrosodurene** (**ND**), **2,4,6-tri-*tert*-butylnitrosobenzene** (***t*-Bu$_3$NB**), **5,5-dimethylpyrroline 1-oxide** (**DMPO**), **methylene-*N*-*tert*-butylnitrone** (**MBN**), and **phenyl-*N*-*tert*-butylnitrone** (**PBN**).

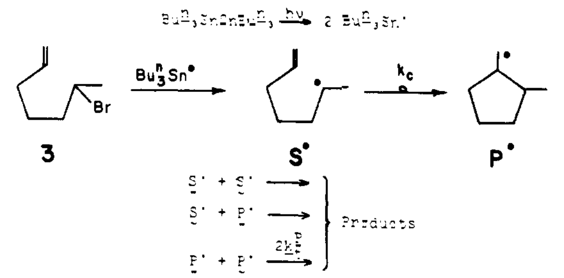
2,6-Di-*tert*-butyl-1,4-benzoquinone (Aldrich) was purified by preparative VPC (5 ft 5% O.V. 101 column at 160 °C) to remove a trace (0.09%) of 2,6-di-*tert*-butyl-4-methoxyphenol. If this was not done, the only EPR signal observed on reaction with diacyl peroxides was that due to 2,6-di-*tert*-butyl-4-methoxyphenoxy.

Measurement of k_c. Although the tin hydride method suggests that 6-hepten-2-yl cyclizes somewhat more rapidly than 5-hexenyl,[6,7] we felt that it would be worthwhile to measure the rate constant, k_c, more accurately and over a range of temperature. The technique employed is that of kinetic EPR spectroscopy which we have used previously to measure the Arrhenius parameters for the cyclization of 5-hexenyl[15,16] and 4-cyanobutyl[17] radicals. The general experimental procedure for studying unimolecular radical reactions by this technique has been adequately described.[15–18]

General Procedure for Spin Trapping. Samples were prepared in quartz EPR tubes by adding aliquots of stock solutions of the spin traps to known quantities of the diacyl peroxide as described previously.[4,5] The degassed, frozen solutions were transferred to the preheated cavity of a Varian E-4 EPR spectrometer. Spectra were recorded as a function of time and ratios of the concentrations of the different spin adducts were determined by double integration of nonoverlapping lines of known degeneracy in the first derivative spectra. The solvent was benzene in all cases and the radicals were produced by *thermal* decomposition of diacyl peroxides. All spin trapping rate measurements were made at 40 °C.

Dimerization of Nitrosodurene. This spin trap is highly dimerized in solution and since only the monomer will be active it is necessary to know the equilibrium constant for dimerization, $K = [\text{dimer}]/[\text{monomer}]^2$. In our earlier work we obtained a value of 16 for ϵ_{750}, the molar extinction coefficient/cm monomer at 750 nm (which is slightly off the band maximum), and a value for $K = 286$ M^{-1} at 22 °C. Assuming that the temperature coefficient of K would be small we estimated $K = 250 \pm 25$ M^{-1} at 40 °C. We subsequently learned that this equilibrium constant had also been measured in benzene at temperatures from 20 to 40 °C by Doba, Ichikawa, and Yoshida.[19] They obtained ϵ_{800} (the band maximum) 91 M^{-1} cm^{-1} and a van't Hoff relation which can be represented as $\log (K/M^{-1}) = -6.80 + 14.5/\theta$, where $\theta = 2.303RT$ kcal/mol. This gives $K = 2140$ M^{-1} at 40 °C. This large discrepancy led to additional studies on this equilibrium. A very careful remeasurement in our laboratory at 22 °C (the only temperature available for experimental reasons) gave $K = 2000 \pm 440$ M^{-1} with ϵ_{800} 47 ± 5 M^{-1} cm^{-1}. Meanwhile, measurements

Scheme I



in Professor Yoshida's laboratory[20] gave ϵ_{800} 36 ± 2 M^{-1} cm^{-1} at 29 °C and, on the assumption that ϵ is temperature independent, the van't Hoff relation, $\log (K/M^{-1}) = (-8.74 \pm 0.10) + (16.1 \pm 3.8)/\theta$ at temperatures from 25 to 40 °C. This equation yields $K = 1565\ M^{-1}$ at 22 °C (which is in satisfactory agreement with our revised value considering the difficulties inherent in these experiments) and $K = 322\ M^{-1}$ at 40 °C. If we combine the two sets of data (without correcting for the different ϵ values) we obtain $\log (K/M^{-1}) = -10.72 + 18.9/\theta$, which yields $K = 303\ M^{-1}$ at 40 °C. It is this last value that we have used in our spin trapping calculations.

Results

Measurement of k_c. The irreversible cyclization of the secondary 6-hepten-2-yl radical, S·, to the primary 2-methylcyclopentylcarbinyl radical, P·, was studied by kinetic EPR spectroscopy. The S· radicals were produced by bromine abstraction from 2-bromo-6-heptene (**3**) using photochemically generated tri-*n*-butyltin radicals in *n*-pentane as the solvent. Absolute concentrations (determined by calibration with DPPH)[21] of S· and P· were measured under steady photolysis at temperatures from 183 to 232 K. The overall reaction can be represented as shown in Scheme I. Since S· and P· are sterically unhindered alkyl radicals of low molecular weight the radical-radical reactions all occur at the diffusion-controlled limit. Under such circumstances the rate constant ratio, $k_c/2k_t^P$, is given by[15-18]

$$k_c/2k_t^P = [P\cdot](1 + [P\cdot]/[S\cdot])$$

The experimentally measured S· and P· concentrations are listed in Table I, together with the derived values of $k_c/2k_t^P$. This data can be represented by

$$\log (k_c/2k_t^P/M) = -(2.0 \pm 0.3) - (4.1 \pm 0.3)/\theta \quad (II)$$

The rate constant for the bimolecular self-reaction of the rearranged radical, $2k_t^P$, was measured by the usual method[21] in *n*-pentane at 240 K. The radical decayed with second-order kinetics and with a rate constant of $4.5_7 \times 10^9\ M^{-1}\ s^{-1}$, which indicates that the reaction is diffusion controlled. The variation in $2k_t^P$ with temperature can therefore be estimated from the temperature coefficient of viscosity of the solvent.[22] It can be represented by

$$\log (2k_t^P/M^{-1}\ s^{-1}) = 11.79 - 2.34/\theta \quad (III)$$

From eq II and III, the rate constant for the S· → P· cyclization can be represented by

$$\log (k_c/s^{-1}) = (9.8 \pm 0.3) - (6.4 \pm 0.3)/\theta \quad (IV)$$

This equation would seem to be fairly reliable since the Arrhenius preexponential factor is in the range found for analogous cyclizations, e.g., $10^{9.5}\ M^{-1}\ s^{-1}$ for 5-hexenyl[16] and $10^{9.9}\ M^{-1}\ s^{-1}$ for 4-cyanobutyl.[17]

Equation IV yields $k_c = 2.1 \times 10^5\ s^{-1}$ at 40 °C, slightly faster than the rate constant for the 5-hexenyl cyclization, which is $1.78 \times 10^5\ s^{-1}$ at this temperature.[16] The ratio of these rate constants is 1.18, in good agreement with values of 1.4 at 40[6] and 65 °C[7] measured by the tin hydride method.[23]

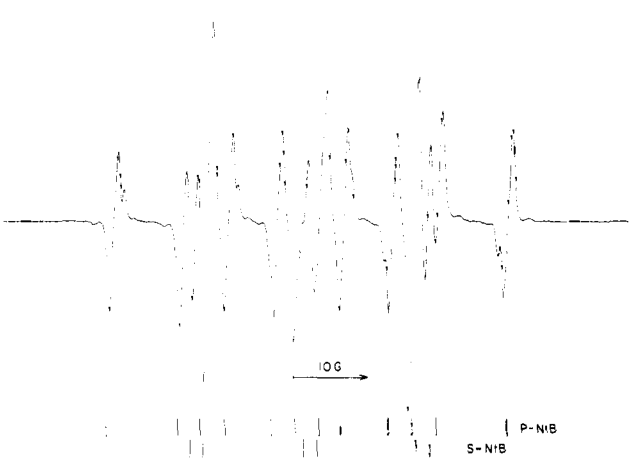
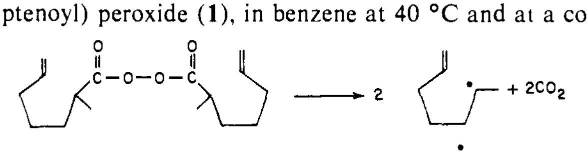


Figure 1. EPR spectrum of adducts formed from **1** (6.1×10^{-3} M) and NtB (1.3×10^{-2} M) in benzene at 40 °C.

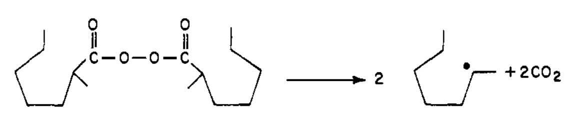
Table I. Radical Concentrations and $k_c/2k_t^P$ Ratio for the Cyclization of 6-Hepten-2-yl Radicals in *n*-Pentane

temp, K	$[S\cdot] \times 10^8$, M	$[P\cdot] \times 10^8$, M	$k_c/2k_t \times 10^7$, M
183	21.6	9.4	1.35
188	19.9	7.1	0.96
192	18.6	10.4	1.62
196	12.6	12.4	2.46
205	8.6	19.4	6.32
209	7.7	19.3	6.77
214	6.9	19.1	7.20
227	5.6	22.4	11.2
232	4.0	22.0	14.3

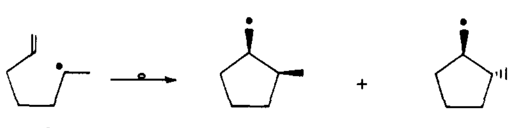
Measurement of k^T. Trapping with 2-Methyl-2-nitrosopropane (NtB). Thermal decomposition of di(2-methyl-6-heptenoyl) peroxide (**1**), in benzene at 40 °C and at a concentration of 6.1×10^{-3} M in the presence of 1.3×10^{-2} M NtB, gave an unexpectedly complex EPR spectrum (see Figure 1). Under the same conditions, di(2-methyl-6-heptanoyl) peroxide (**2**) gave a simple EPR spectrum consisting of a triplet ($a^N = 14.8$ G) of doublets ($a^H = 1.8$ G). This was obviously due to the trapping of the secondary heptan-2-yl radical, H·. With this guide it becomes clear that *two* different primary alkyls are formed from S· and are trapped by the NtB to give spin adducts having slightly different EPR parameters. The formation of two *distinguishable* P–NtB spin adducts is, to us, the surprising result since earlier product studies had already shown the S· cyclizes to give both the *cis*-methyl-, P·$_{cis}$, and *trans*-methyl-, P·$_{trans}$, cyclopentylcarbinyl radicals[25-27] in a



1 **S·**



2 **H**



S· **P·$_{cis}$** **P·$_{trans}$**

Table II. EPR Parameters for Spin Adducts in Benzene at 40 °C (Hyperfine Splittings in Gauss)

spin adduct[a]	a^N	$a^{H\,b}$	*g*
H-NtB	14.8	1.8	2.0059
S-NtB	14.7	1.7	2.0061
P_{cis}-NtB	15.4	12.6 (H_a), 9.5 (H_b)	2.0061
P_{trans}-NtB	15.2	11.3 (H_a),[c] 9.8 (H_b)[c]	2.0061
S-ND	13.6	6.9	2.0061
P-ND[d]	13.3	13.2 (H_a), 9.5 (H_b)	2.0061
S-*t*-Bu_3NB[e]	10.8	1.7 (3 H)[f]	2.0041
S-*t*-Bu_3NB[g]	13.4	22.3	2.0062
P-*t*-Bu_3NB[d,g]	14.1	19.5 (H_a), 13.5 (H_b), 0.8 (2 H_m)	2.0062
H-PBN	14.6	2.5	*h*
H-DMPO	14.2	21.8	*h*
H-MBN	15.2	11.6 (H_a), 9.2 (H_b)	*h*

[a] H = heptan-2-yl, S = hepten-2-yl, P = 2-methylcyclopentylcarbinyl; for spin adduct abbreviations see text. [b] One hydrogen unless otherwise specified. [c] Best values, estimated by computer simulation. [d] Cis and trans P-adduct spectra not resolved. [e] Anilino spin adduct. [f] βH + 2 H_{meta}. [g] Nitroxide spin adduct. [h] Not measured.

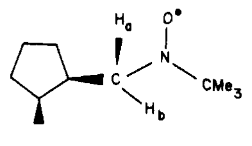
Table III. Spin Trapping 6-Hepten-2-yl, S·, and the Rearranged 2-Methylcyclopentylcarbinyl, P·, Radicals with NtB in Benzene at 40 °C

[NtB] × 10^3, M	$\frac{(d[S\text{-}NtB]/dt)_{t\to0}}{(d[P\text{-}NtB]/dt)_{t\to0}}$[a]	$k^T \times 10^{-5}$,[b] $M^{-1}\,s^{-1}$	$v_i \times 10^9$,[c] $M\,s^{-1}$
4.2	0.133	66.5	1.39
8.4	0.223	55.8	1.19
12.6	0.320	53.3	0.95
16.8	0.456	57.0	1.06
33.6	1.156	72.3	0.94

[a] [P-NtB] = [P_{cis}-NtB] + [P_{trans}-NtB]. [b] Calculated from eq I with $k_c = 2.1 \times 10^5\ s^{-1}$. Average value of $k^T = (61 \pm 8) \times 10^5\ M^{-1}\ s^{-1}$. [c] v_i = d[S-NtB]/d*t* + d[P-NtB]/d*t*. Initial concentration of **1** = 3.05×10^{-3} M.

ratio of ca. 2.7:1[25] to 2,3:1.[26] The ratio of the integrated peak areas of either of the outermost, incompletely resolved, pair of lines shown in Figure 1 is roughly 2.8:1. This allows us to assign the spectrum with the larger (by 1.4 G) overall width to P_{cis}-NtB,

An additional complication in the P_{cis}-NtB (and also in the P_{trans}-NtB) spectrum arises because the β-CH_2 hydrogens are magnetically inequivalent. This is because P_{cis}-NtB, like other analogous nitroxides,[28,29] is chiral by virtue of the asymmetric 2-methylcyclopentyl group. The β-CH_2 hydrogens are therefore inequivalent even if there is rapid internal rotation about the N-C_β bond. The EPR parameters for these and the other spin adducts generated in this work are summarized in Table II.

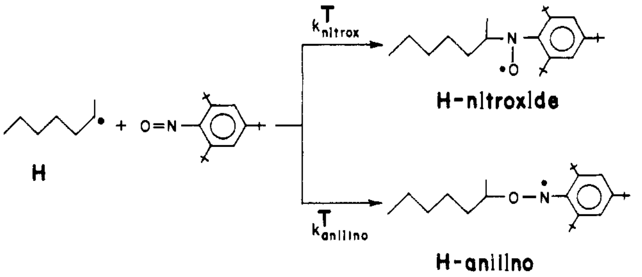


P_{cis}-NtB

The ratios of the initial rates of formation of the S· and P· spin adducts of NtB are given in Table III at various NtB concentrations. Under the experimental conditions employed (for which $k_c = 2.1 \times 10^5\ s^{-1}$) the average value of the rate constant for the trapping of secondary alkyls by NtB is calculated (by eq I) to be $(6.1 \pm 0.8) \times 10^6\ s^{-1}$. In each of these experiments the initial concentration of the diacyl peroxide, **1**, was 3.05×10^{-3} M and the total rate of formation of spin adducts, v_i, was $(1.1 \pm 0.2)10^{-9}\ M^{-1}\ s^{-1}$. Since this rate does not depend on the NtB concentration it is clear that essentially all the alkyl radicals generated are trapped in each experiment. This rate of radical formation yields a rate constant for the decomposition of **1** at 40 °C of $3.0 \times 10^{-7}\ s^{-1}$. The peroxide decomposition is not exactly a "clean" first-order process. Measurements at different peroxide concentrations yield, on extrapolation to zero peroxide concentration, a rate constant of $2.8 \times 10^{-7}\ s^{-1}$.[30]

Trapping with Nitrosodurene (ND). The EPR spectra of the two isomeric cis and trans P-ND adducts cannot be distinguished (see Table II). As is well-known, this nitroso compound is strongly dimerized in solution. The monomer concentration was calculated from the total ND concentration (as monomer) using an equilibrium constant, $K = 303\ M^{-1}$ in benzene at 40 °C (see Experimental Section). The rate constant for trapping was obtained from the ratio of the initial rates of formation of S-ND and P-ND (see Table IV). The values of v_i (at [**1**] = 3.05×10^{-3} M) again indicate that all the alkyl radicals are trapped by the ND.

Trapping with 2,4,6-Tri-*tert*-butylnitrosobenzene (*t*-Bu_3NB). This trap is known to give only nitroxide spin adducts with primary alkyl radicals.[4,32] However, it has been reported[32] that with secondary alkyls both nitroxide and anilino spin adducts are produced. We have confirmed this observation with the secondary alkyls formed by thermal decomposition of both **1** and **2**. Thus, at 40 °C, **2** gives the H-nitroxide and H-anilino spin adducts in a ratio of 0.057, independent of the trap concentration (see Table V).



The absolute rate constant at 40 °C for the spin trapping of secondary alkyls as their anilino adducts was found to be $3.1 \times 10^5\ M^{-1}\ s^{-1}$ by comparison of the rates of formation of the S-anilino and P-nitroxide[33] adducts in the usual way (see Table VI). Combination of this rate constant with the data in Table V yields a value of $0.177 \times 10^5\ M^{-1}\ s^{-1}$ as the rate constant for the trapping of secondary alkyls as their nitroxide adducts.

Competition between Two Spin Traps. The EPR spectra for the ST· and PT· adducts with nitrones are not sufficiently different for k^T values to be measured directly, However, these rate constants can be measured by competitive experiments, as described previously,[4,5] using a trap for which k^T has already been determined. The results of these experiments using H·

Table IV. Spin Trapping S· and P· Radicals with ND in Benzene at 40 °C

total [ND] $\times 10^3$, M	monomer [ND][a] $\times 10^3$, M	$\frac{(d[\text{S–ND}]/dt)_{t\to 0}}{(d[\text{P–ND}]/dt)_{t\to 0}}$	$k^T \times 10^{-5}$,[b] $M^{-1}\,s^{-1}$	$v_i \times 10^9$,[c] $M\,s^{-1}$
1.9	1.3	0.254	411	1.23
20.2	6.68	1.26	395	1.42
40.4	10.0	1.96	412	0.98

[a] Based on $K = 303\ M^{-1}$ (see text). [b] Calculated from eq I with $k_c = 2.1 \times 10^5\ s^{-1}$. Average $k^T = (406 \pm 8) \times 10^5\ M^{-1}\,s^{-1}$. [c] [**1**] = 3.05×10^{-3} M.

Scheme II

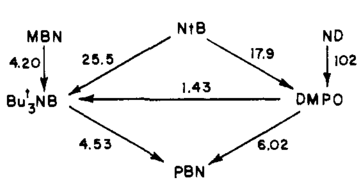


Table V. Spin Trapping H· with *t*-Bu_3NB in Benzene at 40 °C

[*t*-Bu_3NB] $\times 10^3$, M	$\frac{(d[\text{H–nitrox}]/dt)_{t\to 0}}{(d[\text{H–anilino}]/dt)_{t\to 0}}$
3.76	0.0570
7.5	0.0563
30.1	0.0573

Table VI. Spin Trapping S· and P· Radicals with *t*-Bu_3NB in Benzene at 40 °C

[*t*-Bu_3NB] $\times 10^3$, M	$\frac{(d[\text{S–anilino}]/dt)_{t\to 0}}{(d[\text{P–nitrox}]/dt)_{t\to 0}}$	k^T anilino[a] $\times 10^5$, $M^{-1}\,s^{-1}$	$v_i \times 10^9$,[b] $M\,s^{-1}$
30.8	0.054	3.71	0.91
120	0.163	2.86	0.83
308	0.404	2.75	0.98

[a] Calculated from eq I with $k_c = 2.1 \times 10^5\ s^{-1}$. Average $k^T = (3.11 \pm 0.43) \times 10^5\ M^{-1}\,s^{-1}$. [b] [**1**] = 3.05×10^{-3} M.

Table VII. Summary of Rate Constants for Spin Trapping Alkyl Radicals in Benzene

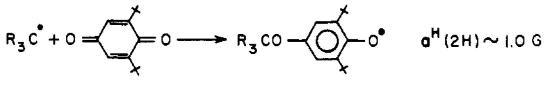
spin trap	$k^T \times 10^{-5}$, $M^{-1}\,s^{-1}$		
	prim[a] 40 °C	sec[b] 40 °C	tert[c] 26 °C
2-methyl-2-nitrosopropane (NtB)	90	61	33
nitrosodurene (ND)	407[d]	406	900[e]
tri-*tert*-butylnitrosobenzene			
(*t*-Bu_3NB)-nitroxide	4.7	0.18	*f*
(*t*-Bu_3NB)-anilino	*f*	3.1	2.3
dimethylpyrroline 1-oxide (DMPO)	26	4.2	*g*
methylene-*tert*-butylnitrone (MBN)	31	13	*g*
phenyl-*tert*-butylnitrone (PBN)	1.3	0.68	<0.1
2,6-di-*tert*-butyl-1,4-benzoquinone	*h*	0.93	*g*

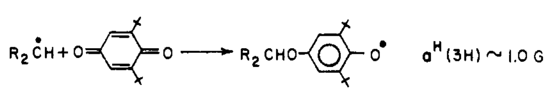
[a] Reference 4. [b] This work. [c] Reference 19. [d] Recalculated taking $K = 303\ M^{-1}$. [e] Revised value, ref 20. [f] Not observed. [g] Not measured. [h] Complex reaction; see text.

radicals from 3.3×10^{-3} M **2** in benzene at 40 °C are summarized in Scheme II. Arrows connect pairs of traps used in competition and point from the more reactive to the less reactive trap. Rate constant ratios are given on each arrow.[34] They are all averages of four or more individual competitive measurements at relative trap concentrations varying by at least an order of magnitude.

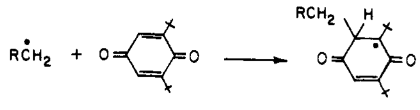
The validity of Scheme II is attested to by its internal consistency and by the satisfactory agreement between these rate constant ratios for the nitroso traps and those obtained using the S· → P· rearrangement. The absolute rate constants for secondary alkyl radical spin trapping by all the foregoing traps are summarized in Table VII.

Trapping with 2,6-Di-*tert*-butyl-1,4-benzoquinone. Roginskii and Belyakov[35] recently reported that this quinone is a useful trap for thermally generated alkyl radicals.[36] The spin adducts formed with a number of tertiary[37] and secondary alkyls showed hyperfine splittings by two (meta) and three (2-meta + α-H of secondary alkyl) equivalent hydrogens, respectively, which indicates that they are the corresponding 4-alkoxy-2,6-di-*tert*-butylphenoxy radicals.





Thermal decomposition of **2** in the presence of this quinone gave the expected adduct having three equivalent hydrogens (a^H (3 H) = 0.9 G). Competition with NtB in benzene at 40 °C yielded a rate constant for the trapping of H· of 0.93×10^5 $M^{-1}\,s^{-1}$, which is somewhat smaller than the value of 8×10^5 $M^{-1}\,s^{-1}$ reported[35] for the secondary alkyl radicals derived from *n*-decane at 50 °C. An attempt to confirm our value via peroxide **1** and the S· → P· rearrangement yielded a complex EPR spectrum (overall width = 3.2 G, six lines) which appeared to derive from more than one radical. A similar, but not quite identical, spectrum was obtained with *n*-heptanoyl peroxide (which yields *n*-hexyl radicals) *and* with acetyl peroxide (methyl radicals). Roginskii and Belyakov[35] also reported that methyl (from the decomposition of *tert*-butoxy) gave a complex spectrum (which is probably not the same as that we obtained). They suggest that one of their observed radicals corresponds to methyl addition to the 3 position of the quinone. The present results suggest that primary alkyls are also sufficiently unhindered to add to this position.[34] Certainly, in the case of benzoquinone itself, primary alkyls add to the ring very rapidly.[40] The rate constant for this reaction has been estimated[40] to be $2 \times 10^7\ M^{-1}\,s^{-1}$ at 69 °C.



Trapping Tertiary Alkyl Radicals. We could not devise an unequivocal method for measuring k^T for tertiary alkyl radicals. However, *relative* k^T values were obtained for the tertiary 2-phenylprop-2-yl (cumyl) radical which was generated by the thermal decomposition of azocumene[41,42] in benzene at 40 °C in the presence of pairs of spin traps.

$$C_6H_5C(CH_3)_2N{=}NC(CH_3)_2C_6H_5 \rightarrow 2C_6H_5\dot{C}(CH_3)_2 + N_2$$

These data are summarized in Table VIII together with *relative* k^T values for the primary and secondary alkyl radicals. In comparing the relative k^T values for these three types of radical, it must be remembered that the primary and secondary

Table VIII. Relative Rate Constants for Spin Trapping Alkyl Radicals in Benzene at 40 °C

spin trap	prim[a] 5-hexenyl	sec[a] 6-hepten-2-yl	tert[b] cumyl
NtB	(100)[c]	(100)[c]	(100)[c]
ND	450	670	110
t-Bu_3NB-nitroxide	5.2	0.3	
t-Bu_3NB-anilino		5.1	4.8
DMPO	29	6.9	1.9[d]
MBN	34	21	12
PBN	1.4	1.1	0.0027[d]

[a] From Table VII. [b] This work. [c] Assumed. [d] For the cumyl radical (k^T)DMPO/(k^T)PBN ≈ 700. However, under the same experimental conditions the less hindered $(CH_3)_2\dot{C}CN$ radical (derived from azobisisobutyronitrile) gave a ratio of only ca. 34.

radicals are nonstabilized alkyls whereas the tertiary is a resonance-stabilized benzylic radical.[43]

Discussion

The absolute rate constants for the spin trapping of secondary alkyl radicals in benzene at 40 °C are summarized in Table VII. As with the trapping of primary alkyls[4] relative k^T values are probably accurate to ±30% but absolute values are probably reliable to no more than a factor of 2. The present data are compared with the rate constants measured previously for trapping primary alkyls under the same conditions[4] and with those reported by Doba et al.[19] for *tert*-butyl trapping in benzene at 26 °C. In the latter work the *tert*-butyl radicals were generated by photolysis of the 2-methyl-2-nitrosopropane spin trap. The relative rate constants obtained in competitive experiments were put on an absolute scale by an intermolecular competition with a reaction having a known rate constant, viz., H-atom abstraction by *tert*-butyl from tri-*n*-butyltin hydride.[24] We believe that our own experimental procedure is inherently the more reliable. However, there is obviously general agreement between our results and those of Doba et al.[19] (see Table VII), which is extremely gratifying. The overall picture for primary, secondary, and tertiary alkyl radicals reveals that, with one exception, $k^T_{prim} > k^T_{sec} > k^T_{tert}$, just as would be expected (see Table VII). The one exception is ND, which is by far the most reactive trap, and we presume that experimental problems have hidden a similar trend in this case.

The relative reactivities of the various spin traps toward secondary alkyls (see Table VIII) are rather similar to those found for primary alkyls and discussed previously.[4] The most surprising result is the relatively low reactivity of PBN toward the cumyl radical. This might be due to steric factors (cf. footnote *d*, Table VIII) or to the fact that cumyl is a resonance-stabilized alkyl radical.

Tri-*tert*-butylnitrosobenzene is an extremely interesting trap because the [(*t*-Bu_3NB)-nitroxide]/[*t*-Bu_3NB)-anilino] spin adduct ratio, γ, is so highly dependent on the steric bulk of the attacking alkyl radical. Even with secondary alkyls γ is not a constant. Thus, with hept-2-yl $\gamma = 0.057$, whereas Terabe and Konaka[32] have reported γ values of 0.5 and 3 for *n*-Pr$\dot{C}$HOH and Et$\dot{C}$HOH, respectively, while Me$\dot{C}$HOH gave only the nitroxide adduct. Another interesting result is that the *total* rate constant for trapping hept-2-yl (viz., 3.28×10^5 M^{-1} s^{-1}) is not much smaller than the rate constant for trapping a primary alkyl (viz., 4.7×10^5 M^{-1} s^{-1}). It would appear, therefore, that the steric influence of the two ortho *tert*-butyl groups manifests itself primarily as a "directing" effect and only to a much lesser extent does it retard the rate of radical addition (cf. also relative and "absolute" values of k^T for tertiary alkyls). The possibility that primary alkyls also yield some anilino radicals initially, but that these rearrange rapidly to the nitroxide, cannot be entirely ignored.

Future work in this field will be directed toward measuring the rates of trapping of heteroatom-centered free radicals.

Acknowledgment. We are extremely grateful to Mrs. A. Martin and Dr. H. H. Mantsch for kindly measuring the monomer–dimer equilibrium constant for nitrosodurene, and to Professor H. Yoshida for much helpful correspondence on this topic and for communicating his unpublished results to us. We should also like to thank Professors E. G. Janzen and L. R. C. Barclay for some of the spin traps and their helpful comments while this work was in progress. One of us (K.U.I.) also acknowledges stimulating discussions on spin trapping with Professor L. Lunazzi which were made possible by a NATO Research Grant. Thanks are also due to Professor J. K. S. Wan for communicating his results on spin trapping with quinones prior to publication.

References and Notes

(1) Issued as N.R.C.C. No. 17612. Part 33: Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.*, **1979,** *101*, 837.
(2) N.R.C.C. Research Associate, 1977–1979.
(3) For reviews of spin trapping see Perkins, M. J. *Chem. Soc.*, *Spec. Publ.* **1970,** *No. 24*, **97**. Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31. Janzen, E. G. "Free Radicals in Biology", Vol. 4, Pryor, W. A., Ed.; Academic Press: New York, in press.
(4) Schmid, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1978,** *100*, 2493.
(5) Maeda, Y.; Schmid, P.; Griller, D.; Ingold, K. U. *J. Chem. Soc., Chem. Commun.* **1978,** 525.
(6) Walling, C.; Coiffari, A. *J. Am. Chem. Soc.* **1972,** *94*, 6059.
(7) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974,** 2251.
(8) Ingold, K. U. "Free Radicals", Vol. 1; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 2.
(9) In the later stages the alkyl radicals will also react with the spin adducts.[4]
(10) Lund, H.; Bjerrum, J. *Chem. Ber.* **1931,** *64B*, 210.
(11) Attempts to decarboethoxylate the malonic ester by the procedure of Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* **1973, 957**, were unsuccessful. This reaction was too slow even at the boiling point of Me_2SO (189 °C).
(12) Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1962,** *1*, 351.
(13) Mair, R. D.; Graupner, A. J. *Anal. Chem.* **1964,** *36*, 194.
(14) Johnson, W. S.; Owyang, R. *J. Am. Chem. Soc.* **1964,** *86*, 5593.
(15) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974,** *96*, 6355.
(16) Schmid, P.; Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.*, **1979,** *11*, 333.
(17) Griller, D.; Schmid, P.; Ingold, K. U. *Can. J. Chem.*, **1979,** *57*, 831.
(18) Griller, D.; Roberts, B. P. *Chem. Commun.* **1971,** 1035. *J. Chem. Soc., Perkin Trans. 2* **1972,** 747. Davies, A. G.; Griller, D.; Roberts, B. P. *ibid.* **1972, 99**3. Watts, G. B.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1972,** *94*, 8784. Maillard, B.; Ingold, K. U. *ibid.* **1976,** *98*, 1224. Maillard, B.; Forrest, D.; Ingold, K. U. *ibid.* **1976**, *98*, 7024.
(19) Doba, T.; Ichikawa, T.; Yoshida, H. *Bull. Chem. Soc. Jpn.* **1977,** *50*, 3158.
(20) Yoshida, H.; Doba, T. *Bull. Fac. Eng., Hokkaido Univ.*, **1978,** *91*, 161. See also Doba, T.; Noda, S.; Yoshida, H. *Bull. Chem. Soc. Jpn.* **1979,** *52*, 21.
(21) See e.g., Adamic, K.; Bowman, D. F.; Gillan, T.; Ingold, K. U. *J. Am. Chem. Soc.* **1971,** *93*, **903**.
(22) Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1976,** *8*, 341. *Helv. Chim. Acta* **1978,** *61*, 2130.
(23) This method relies on measuring the yields of open-chain and cyclized hydrocarbons produced when the open-chain bromide is reduced with tri-*n*-butyltin hydride. However, in order to compare the cyclization of a secondary alkyl with that of a primary alkyl it is necessary to rely on Carlsson and Ingold's[24] absolute rate constants for the alkyl radical–*n*-Bu_3SnH reaction. At 25 °C these were 1×10^6, 1.2×10^6, and 0.74×10^6 M^{-1} s^{-1} for *n*-hexyl, cyclohexyl, and *tert*-butyl. The secondary alkyl result is anomalous.[24] If the rate constant for an acyclic secondary alkyl were ca. 1×10^6 M^{-1} s^{-1} then the tin hydride data would be in agreement with the EPR results.
(24) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968,** *90*, 7047.
(25) Brace, N. O. *J. Org. Chem.* **1967,** *32*, 2711.
(26) Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974,** *96*, 1613.
(27) See also Kuehn, M. E.; Damon, R. E. *J. Org. Chem.* **1977,** *42*, 1825.
(28) Tordo, P.; Bertrand, M. P.; Surzur, J. M. *Tetrahedron Lett.* **1970, 1799**. Flesia, E.; Croatto, A.; Tordo, P.; Surzur, J. M. *ibid.* **1972,** 535. Taniguchi, H.; Hatano, H. *Chem. Lett.* **1975, 9**. Joshi, A.; Rustgi, S.; Riesz, P. *Int. J. Radiat. Biol.* **1976,** *30*, 151. Rustgi, S.; Joshi, A.; Moss, H.; Reisz, P. *ibid.* **1977,** *31*, 415. Rustgi, S.; Joshi, A.; Riesz, P.; Friedburg, F. *ibid.* **1977,** *32*, 533. Rustgi, S., Riesz, P. *ibid.* **1978,** *33*, 21, 325. **1978,** *34*, 127, 149. Joshi, A.; Rustgi, S.; Moss, H.; Riesz, P. *ibid.* **1978,** *33*, 205. Joshi, A.; Moss, H.; Riesz, P. *ibid.* **1978,** *34*, 165. Kominami, S.; Rokushika, S.; Hatano, H. *ibid.* **1976,** *30*, 525. *Radiat. Res.* **1977,** *72*, 89. Rustgi, S.; Riesz, P. *ibid.* **1978,** *75*, 1.
(29) And, of course, other $XCH_2\dot{C}(Y)Z$ radicals in which X is asymmetric; see,

e.g., Gilbert, B. C.; Trenwith, M. *J. Chem. Soc., Perkin Trans. 2* **1973,** 1834. Lagercrantz, C.; Setaka, M. *Acta Chem. Scand., Ser. B.* **1974,** *28*, 619. Smith, P.; Stevens, R. D.; Gilman, L. G. *J. Phys. Chem.* **1975,** *79*, 2688. Ashworth, B.; Gilbert, B. C.; Smith, P.; Stevens, R. D.; Kaba, R. A. *J. Magn. Reson.* **1975,** *19*, 398. Smith, P.; Gilman, L. G.; Stevens, R. D.; de Hargrave, C. V. *ibid.* **1978,** *29*, 545.

(30) The rate constant for thermal decomposition of *n*-alkanoyl peroxides can be calculated[31] to be *ca.* 2.2×10^{-7} s^{-1} at 40 °C. Secondary alkanoyl peroxides probably decompose somewhat more rapidly than the primary peroxides.

(31) Guillet, J. E.; Walker, T. R.; Meyer, M. F.; Hawk, J. P.; Towne, E. B. *Ind. Eng. Chem., Prod. Res. Dev.* **1964,** *3*, 257.

(32) Terabe, S.; Konaka, R. *J. Chem. Soc., Perkin Trans. 2* **1973,** 369.

(33) P_{cis} and P_{trans} nitroxides were not distinguishable.

(34) Ratios involving *t*-Bu_3NB refer to the anilino adduct only.

(35) Roginskii, V. A.; Belyakov, V. A. *Dokl. Akad. Nauk SSSR* **1977**, *237*, 1404.

(36) Radical addition to quinones has long been known; see e.g., Waters, W. A. "The Chemistry of Free Radicals", Clarendon Press: Oxford, 1946; p 49.

(37) The trapping of thermally generated *tert*-butyl radicals has been independently confirmed (Chen, K. S.; Foster, T.; Wan, J. K. S. Private communication). This quinone would also appear to have great potential as a spin trap for metal-centered radicals.

(38) Alkyl addition to the 4 position followed by a ring expansion is another possibility suggested by recent work by Nishinaga et al.[39]

(39) Nishinaga, A.; Itahara, T.; Shimizu, T.; Matsuura, T. *J. Am. Chem. Soc.* **1978,** *100*, 1820. Nishinaga, A.; Itahara, T.; Matsuura, T.; Rieker, A.; Koch, D.; Albert, K.; Hitchcock, P. B. *ibid.* **1978,** *100*, 1826. Nishinaga, A.; Nakamura, K.; Matsuura, T. *Tetrahedron Lett.* **1978,** 3557, 3597. Nishinaga, A.; Shimizu, T.; Matsuura, T. *ibid.* **1978,** 3747.

(40) Citterio, A. *Tetrahedron Lett.* **1978,** 2701.

(41) Nelsen, S. F.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966,** *88*, 137.

(42) There were some problems with $CH_3\cdot$ radical trapping. These were overcome by recrystallization of the azocumene. The original material must have contained a source of cumyloxy radicals.

(43) Attempts to measure relative k^T values for $Me_3C\cdot$ generated by thermal decomposition of $Me_3COOC(O)CMe_3$ were frustrated by the simultaneous formation of $Me_3CO\cdot$ and $Me\cdot$ spin adducts with several of the traps. We were unable to prepare pure $Me_3CC(O)OOC(O)CMe_3$.

Mechanism of Reductive Elimination. Reaction of Alkylpalladium(II) Complexes with Tetraorganotin, Organolithium, and Grignard Reagents. Evidence for Palladium(IV) Intermediacy

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Abstract: Coupling products are obtained in good yields from the reaction of tetraorganotin compounds or Grignard reagents and organohalogenopalladium(II) complexes provided that a benzyl bromide is present. Low yields are obtained in the absence of the benzyl bromides, in which case other decomposition pathways (e.g., α elimination) take place, even in the presence of electron acceptors (e.g., oxygen, *m*-dinitrobenzene). The first step in the reaction of benzylhalogenobis(triphenylphosphine)palladium(II) complexes with MeM (M = $SnMe_3$, MgBr) is metathesis of the benzyl ligand rather than the halogen. This unique carbon-for-carbon transmetalation takes place at 25 °C and is facilitated by electron-donating substituents on the benzyl ligand. The products of this reaction subsequently react at higher temperature in the presence of a benzyl bromide to afford ethylbenzene. Optically active chloro-(α-deuteriobenzyl)bis(triphenylphosphine)palladium yields, upon reaction with tetramethyltin in the presence of *p*-nitrobenzyl bromide, optically active α-deuterioethylbenzene in which overall retention of configuration at carbon has resulted. *cis*-Dimethylbis(triphenylphosphine)palladium(II) reacts with benzyl bromide at 25 °C to afford ethylbenzene and bromomethylbis(triphenylphosphine)palladium(II) rather than ethane. When optically active α-deuteriobenzyl bromide is used in this reaction, optically active α-deuterioethylbenzene is formed, and inversion of configuration at carbon takes place. The reductive elimination process is proposed to take place preferentially from a palladium(IV) intermediate with retention of configuration at carbon.

Introduction

Reductive elimination is a crucial step in low-energy transition-metal mediated transformations of organic compounds to products in which new carbon–carbon bonds have been generated.[1,2] Although there is considerable mechanistic information on oxidative addition reactions of organic compounds to low valent transition-metal complexes,[3-5] there is much less information concerning the reverse, reductive elimination reaction.

Trialkyltriphenylphosphinegold complexes reductively eliminate cis methyl groups by a first-order process.[6] Diaryl-[7] and arylmethylbis(triphenylphosphine)nickel complexes[7,8] decompose to give coupled products. However, the rate of the entire catalytic cycle is faster than the simple reductive elimination step of two organic groups attached to nickel, so that an induction of the reductive elimination by a prior electron-transfer process from nickel has been proposed.[8] Diarylbis(phosphine)platinum complexes decompose by a concerted coupling mechanism, as evidenced by the absence of crossover products or products derived from radical intermediates.[9]

Reductive elimination reactions also take place with six-coordinate di- and trialkylplatinum(IV) complexes.[10] In certain other di- or trimethyl metal complexes, α elimination is observed instead.[11] Dinuclear reductive elimination takes place in osmium clusters.[12] Critical mechanistic studies on the reductive elimination of diorganopalladium complexes are scarce,[7,13] yet palladium has been demonstrated to catalyze a large number of different coupling reactions in which the reductive elimination step probably has a crucial role.[14]

Results and Discussion

Reactions of Benzylpalladium Complexes with Methyllithium and with Tetramethyltin. (a) Reactions. With the purpose of studying the stereochemistry of reductive elimination from palladium(II) complexes, a study of the sequence outlined in Scheme I was undertaken.

The oxidative addition of optically active α-deuteriobenzyl chloride to tetrakis(triphenylphosphine)palladium(0) (**1**) is known[15] to proceed with 74% net inversion of configuration at the benzylic carbon, whereas the oxidative addition of

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