by about a factor of 4. Indeed, a pair of competitive experiments involving the reaction of CH_3I with n-Bu_3SnH/n-Bu_3SnD and n-Bu_3SnD/n-Bu_3GeH showed that the tin hydride was 18 times more reactive than the germanium hydride at room temperature.[12] Since this difference in reactivity is similar to the factor of 24 (i.e., k_3/k_5) found for primary alkyl radicals we suggest that the $CH_3\cdot$ + n-Bu_3GeH reaction has a room-temperature rate constant of about 5×10^5 M^{-1} s^{-1}. Since n-Bu_3GeH has about $^1/_{20}$ the reactivity of the corresponding tin hydride toward methyl and primary alkyl radicals, it should prove useful as a probe for slow alkyl radical rearrangements.

Acknowledgment. We should like to thank Dr. P. J. Stang and Dr. M. R. White for a generous gift of tri-*n*-butylgermanium hydride. Two of us (B.M. and K.U.I.) acknowledge receipt of a N.A.T.O. Research Grant without which the present work would not have been undertaken.

Registry No. Tri-*n*-butylgermanium hydride, 998-39-0; 5-hexenyl bromide, 2695-47-8; 5-hexenyl, 16183-00-9.

Supplementary Material Available: Two kinetic (Tables II and III) giving detailed kinetic data (3 pages). Ordering information is given on any current masthead page.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 41. Diethoxyphosphonyl Radicals[1]

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Abstract: Rate constants for the abstraction of halogen atoms by diethoxyphosphonyl radicals from some organic halides have been determined by EPR spectroscopy using competitive methods. Some typical rate constants (M^{-1} s^{-1} units) at ambient temperatures in di-*tert*-butyl peroxide/diethyl phosphite (4:1, v/v) as solvent follow: *tert*-butyl chloride, 3.5×10^2; *n*-butyl bromide, 1.0×10^4; *tert*-butyl bromide, 3.0×10^5; benzyl bromide, 1.2×10^6. Diethoxyphosphonyl radicals are less reactive in halogen atom abstractions than triethylsilyl or tri-*n*-butyltin radicals.

Although dialkoxyphosphonyl radicals, $(R'O)_2\dot{P}O$, have long been recognized as intermediates in some reactions of dialkyl phosphites,[3] they were not identified by EPR spectroscopy in solution until 1972.[4] At that time, it was shown that the EPR spectrum due to the $(R'O)_2\dot{P}O$ radical could be replaced by that of an alkyl radical upon the addition of certain alkyl halides to the system.[4] This implies that diethoxyphosphonyl radicals, for example, can abstract halogen atoms fairly readily:

$$(EtO)_2\dot{P}O + RX \rightarrow (EtO)_2P(O)X + R\cdot \qquad (1)$$

Advantage has occasionally been taken of reaction 1 to generate site-specific alkyl radicals for study by EPR spectroscopy.[5] However, for such purposes it has been far more common to employ either trialkylsilyl radicals[6,7] or trialkyltin radicals[7-9] as the halogen-abstracting agents:

$$R'_3Si\cdot + RX \rightarrow R'_3SiX + R\cdot \qquad (2)$$

$$R'_3Sn\cdot + RX \rightarrow R'_3SnX + R\cdot \qquad (3)$$

Since there are now quite extensive lists of absolute rate constants for reaction 2 for R′ = Et,[10] and for reaction 3 for R′ = *n*-Bu,[11] we decided to measure some absolute rate constants for reaction 1 since this would permit quantitative comparison of these three reactions. In the earlier kinetic studies,[10,11] the rate constants for reaction 2 were determined by laser flash photolysis and those for reaction 3 by the rotating sector technique. Neither procedure proved suitable for reaction 1. The laser flash photolytic technique relies on an essentially "instantaneous" generation of the radical in question. This could just be achieved for $Et_3Si\cdot$ radicals in a di-*tert*-butyl peroxide/triethylsilane mixture. However, relatively high silane concentrations were required since the rate constant for H-atom abstraction from the silane by *tert*-butoxyl radicals is only 5.7×10^6 M^{-1} s^{-1} at 300 K.[12] For diethyl phosphite the comparable reaction (4) can be estimated to have a rate constant

$$Me_3CO\cdot + (EtO)_2P(O)H \rightarrow Me_3COH + (EtO)_2\dot{P}O \qquad (4)$$

of ca. 5×10^5 M^{-1} s^{-1} at room temperature,[13] which is much too slow for the "instantaneous" generation of diethoxyphosphonyl.[16] The rotating sector technique relies on the occurrence of a chain reaction of considerable chain length. Such a process does not occur between diethyl phosphite and alkyl halide at ambient temperatures.

For the above reasons values of k_1 were determined by kinetic EPR spectroscopy.[1,17,18] Competitive methods were employed,

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[13] A value for k_4 of ca. 2×10^4 M^{-1} s^{-1} at 263 K has been reported,[14] which would correspond to ca. 5.5×10^4 M^{-1} s^{-1} at room temperature. However, this value was based on an estimated rate constant of 1×10^5 M^{-1} s^{-1} at 303 K for H-atom abstraction from cyclopentane by *tert*-butoxy radicals. The rate constant for this latter reaction has now been measured and found to be 8.8×10^5 M^{-1} s^{-1} at room temperature.[15]

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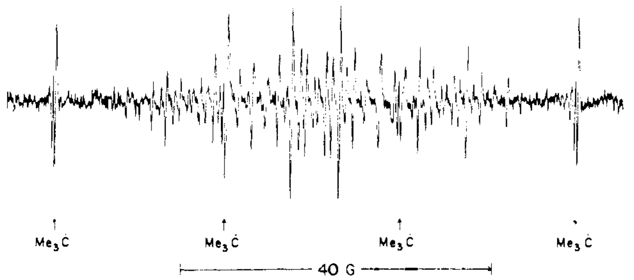

Figure 1. EPR spectrum obtained by photolysis of 0.26 M *tert*-butyl bromide and 0.088 M benzyl bromide in $(EtO)_2P(O)H/Me_3COOCMe_3$ (1:4, v/v) at room temperature. Flow rate = 1.05 mL/min. Modulation amplitude = 0.125 G. Microwave power = 1.0 mW. The marked lines due to the *tert*-butyl radical show second-order effects.

but because of the design of our flow system k_1 values were determined only at room temperature.

Kinetic EPR spectroscopy has been employed in the only two previous measurements of the rate constants for reactions of diethoxyphosphonyl radicals.[19,20] These reactions were the bimolecular self-reaction (eq 5)[19] and the addition to benzene (eq 6).[20]

$$(EtO)_2\dot{P}O + (EtO)_2\dot{P}O \rightarrow \text{nonradical products} \qquad (5)$$

$$(EtO)_2\dot{P}O + C_6H_6 \rightarrow (EtO)_2P(O)C_6H_6\cdot \qquad (6)$$

Experimental Section

Materials. All compounds used were commercially available. Initial experiments in static systems showed that "impurity" transient radicals were produced and that there was a rapid buildup of "impurity" persistent radicals. Such impurity radicals remained a problem even in the flow system unless great precautions were taken to purify the materials. Diethyl phosphite and the organic halides were carefully purified by distillation. The di-*tert*-butyl peroxide, which was used as the solvent, was washed with aqueous $AgNO_3$ to remove olefinic impurities and then with water. It was dried over $MgSO_4$ and finally passed through a column of alumina to remove hydroperoxide impurities.

Apparatus and Procedures. Diethoxyphosphonyl radicals were generated from a 20% (v/v) solution of $(EtO)_2P(O)H$ in di-*tert*-butyl peroxide by direct photolysis in the cavity of a Varian E-104 EPR spectrometer. The solution was first deoxygenated with a stream of N_2 bubbles at 0 °C and was then drawn into a 30-mL hypodermic syringe. A syringe pump (Sage Instruments, Model 355) was used to force the liquid upward through a Supracil-quartz, flat cell (ca. 0.8 mm thickness), which was centered in the EPR cavity with an orientation normal to the incident light. The photolysis source was a Hanovai 977 B-1 Xe–Hg short-arc lamp, which was mounted in a parabolic quartz reflector that focussed the light onto the sample in the cavity.[21] The light was filtered through a cooled aqueous solution of cobalt and nickel sulfates to remove much of the visible and most of the infrared radiation.[23] Under optimum conditions (i.e., 100% light intensity) a total radical concentration of ca. 1.1×10^{-6} M was obtained with this system.

Relative values of k_1 for various pairs of alkyl halides were determined by a series of competitive experiments. The two halides were added to the $(EtO_2)P(O)H/Me_3COOCM_3$ solution, and their relative concentrations were adjusted until the EPR spectra of both alkyl radicals could be observed simultaneously with spectrometer settings of relatively low modulation amplitude (ca. 0.125 G) and microwave power (ca. 1.0 mW), (see Figure 1). In such experiments the total halide concentration was always more than sufficient to eliminate the EPR spectrum due to the phosphonyl radicals; i.e., all of the phosphonyl radicals generated reacted with the halides to form alkyl radicals. Relative alkyl radical concentrations, from which relative k_1 values can be calculated (vide infra), were determined by double integration of appropriate lines in the spectra. In order to minimize errors in concentration that might otherwise arise from polarization of the EPR signals, equivalent pairs of lines from both the high- and low-field region of each spectrum were integrated.

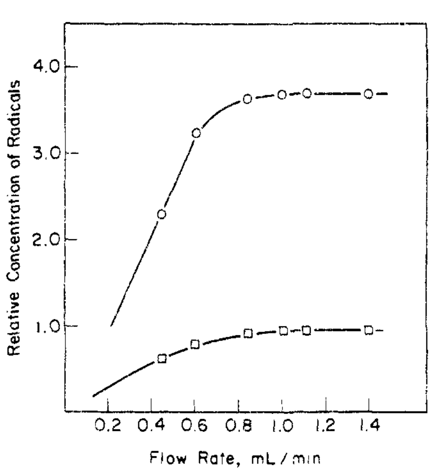

Figure 2. Relative concentration of *n*-butyl (○) and *tert*-butyl (□) radicals as a function of flow rate for [*n*-butyl bromide] = 0.28 M and [*tert*-butyl chloride] = 1.89 M. A flow rate of 1.0 mL/min corresponds to a dwell time in the cell of ca. 6 s.

At flow rates less than ca. 1 mL/min the relative and absolute concentrations of the alkyl radicals were dependent on the flow rate (see Figure 2) because of consumption of one or both substrates. For this reason, radical concentrations were determined only under conditions where the concentration was independent of the flow rate (generally at rates ≥0.85 mL/min).

Relative k_1 values were placed on an absolute scale by measuring k_1 for *tert*-butyl chloride. This compound is sufficiently unreactive toward diethoxyphosphonyl radicals that with 1.07 M *tert*-butyl chloride in $(EtO)_2P(OH)/Me_3COOCMe_3$ (1:4 v/v) as solvent, an EPR spectrum showing both the *tert*-butyl radical and the $(EtO)_2\dot{P}O$ radical could be readily obtained.[24] Measurements of the absolute concentrations of the *tert*-butyl and phosphonyl radicals were made in the usual way[25] by double integration of first derivative lines in the EPR spectra and calibration against the spectrum obtained with benzene solution of DPPH of known concentration (ca. 10^{-4} M), the spectrometer's sensitivity being monitored by the signal from a crystal of synthetic ruby. Different light intensities, produced by inserting wire mesh screens in the light beam, were used to produce different total radical concentrations. The data obtained in this way allow the rate constant ratio, $2k_7/k_1$, where $2k_7$ is the rate constant for the bimolecular self-reaction of *tert*-butyl radicals, to be calculated (vide infra).

$$Me_3C\cdot + Me_3C\cdot \rightarrow \text{nonradical products} \qquad (7)$$

Reaction 7 is diffusion controlled,[11,17,26-30] and values of $2k_7$ have been carefully measured by Fischer and co-workers[28-30] in a variety of solvents. Instead of measuring $2k_7$ (which would be difficult in this system because of the presence of the phosphonyl radical) we therefore measured the viscosity of the $(EtO)_2P(O)H/Me_3COOCMe_3/Me_3CCl$ solution using a Hewlett-Packard Auto-Viscometer, Model 590/B, with cyclohexane as the reference solution. At 298 K the viscosity was 0.848 cP, which is virtually identical with that of *n*-decane at this temperature, viz.[31] 0.854 cP. At room temperature (ca. 295 K) $2k_7$ can therefore be assigned a value of 5.6×10^9 M^{-1} s^{-1}.[29]

Results

Under flow conditions, the continuous UV photolysis of a solution in di-*tert*-butyl peroxide of diethyl phosphite and two alkyl

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Table I. Relative Reactivities of Alkyl Halides toward $(EtO)_2\dot{P}O$ Radicals at 295 K

R_AX, M	R_BY, M	flow rate, mL/min	$[R_A\cdot]/[R_B\cdot]$[a]	$k_1^{R_AX}/k_1^{R_BY}$ [b]
$CH_3(CH_2)_3Br$	$(CH_3)_3CCl$			
0.28	1.89	0.85	4.19	28.3
		1.04	3.88	26.2
		1.40	4.00	27.0
0.42	1.86	0.85	5.91	26.2
		1.05	6.01	26.6
		1.40	6.04	26.7
		1.70	5.95	26.4
				av 26.8 ± 0.70
$CH_3(CH_2)_3Br$	$\overline{(CH_2)_4CH}Br$			
4.84	0.22	0.85	2.90	0.132
		1.05	2.73	0.124
		1.40	2.91	0.132
				av 0.129 ± 0.002
$CH_3(CH_2)_3Br$	$(CH_3)_3CBr$			
1.96	0.039	0.85	1.67	0.0332
		1.70	1.61	0.0320
2.88	0.054	1.05	1.76	0.0330
		1.16	1.76	0.0330
		1.40	1.76	0.0330
				av 0.328 ± 0.0016
$(CH_3)_3CBr$	$\overline{(CH_2)_4CH}Br$			
0.030	0.35	0.85	0.337	3.93
		1.05	0.341	3.98
		1.40	0.336	3.92
0.43	0.80	1.15	2.07	3.85
		1.45	2.12	3.94
				av 3.92 ± 0.052
$(CH_3)_3CBr$	$CH_3CH_2CHBrCH_3$			
0.10	0.75	0.85	0.515	3.86
		1.70	0.515	3.86
0.11	0.82	0.85	0.505	3.76
		1.16	0.513	3.82
				av 3.83 ± 0.19
$(CH_3)_3CBr$	$C_6H_5CH_2Br$			
0.20	0.056	0.85	0.88	0.246
		1.05	0.95	0.266
		1.25	0.88	0.246
		1.40	0.87	0.244
0.21	0.055	0.85	1.01	0.265
				av 0.252 ± 0.011
$(CH_3)_3CBr$	$CH_2{=}CHCH_2Br$			
0.58	0.056	0.85	2.57	0.248
		1.05	2.70	0.261
		1.40	2.71	0.262
				av 0.257 ± 0.007

[a] $[R_A\cdot] + [R_B\cdot] \approx 1.1 \times 10^{-6}$ M in all cases. [b] Errors given on mean values of $k_1^{R_AX}/k_1^{R_BY}$ for each R_AX/R_BY pair are random errors only and correspond to one standard deviation.

halides, R_AX and R_BY, at appropriate concentrations yields EPR spectra for both alkyl radicals, $R_A\cdot$ and $R_B\cdot$. These radicals are destroyed by bimolecular processes, and the overall steady-state system can be represented by reaction 4 followed by

$$(EtO)_2\dot{P}O + R_AX \rightarrow (EtO)_2P(O)X + R_A\cdot \tag{1A}$$

$$(EtO)_2\dot{P}O + R_BY \rightarrow (EtO)_2P(O)Y + R_B\cdot \tag{1B}$$

$$R_A\cdot + R_A\cdot \rightarrow \text{nonradical products} \tag{8}$$

$$R_A\cdot + R_B\cdot \rightarrow \text{nonradical products} \tag{9}$$

$$R_B\cdot + R_B\cdot \rightarrow \text{nonradical products} \tag{10}$$

Table II. Effect of Light Intensity on *tert*-Butyl Radical and Diethoxyphosphonyl Radical Concentrations[a]

relative intensity	$10^7[Me_3C\cdot]$, M	$10^7[(EtO)_2\dot{P}O]$, M
100%	2.15	11.3
100%	2.13	11.2
46.5%	1.63	5.53
38.5%	1.36	3.62
38.5%	1.36	3.62
12.2%	1.01	1.78

[a] $[Me_3CCl] = 1.07$ M in $(EtO)_2P(O)H/Me_3COOCMe_3$ 1:4, v/v, at room temperature.

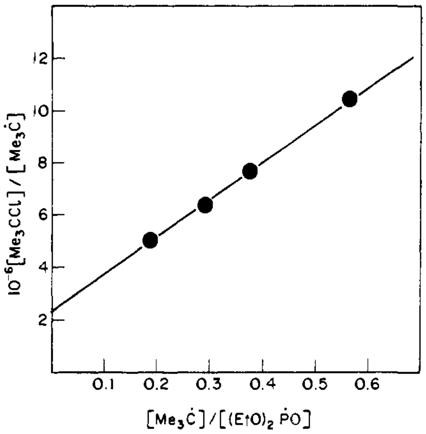

Figure 3. Data from Table II plotted according to eq 14.

Since it is now well established that the bimolecular self-reactions of all simple alkyl radicals[11,17,26-30,32,33] and their cross-reactions[34] proceed at the diffusion-controlled limit (which means that $k_8 = k_9 = k_{10}$), this scheme yields the relation

$$\frac{k_1^{R_AX}}{k_1^{R_BY}} = \frac{[R_BY][R_A\cdot]}{[R_AX][R_B\cdot]} \tag{11}$$

The experimental data that allow rate constant ratios to be calculated according to this equation are given in Table I. We were, however, unsuccessful in our attempts to measure the relative reactivities of quite a number of organic halides. Thus, for example, cyclopentyl chloride was too unreactive, allyl chloride and benzyl chloride gave rather poor signals even at high flow rates because of the rapid formation of yellow colored materials, which absorbed too much of the UV light, and methyl iodide gave the methyl radical by direct photolysis.

The results obtained with *tert*-butyl chloride as the only organic halide are given in Table II. Under the conditions used for this experiment we can write:

$$\frac{d[Me_3C\cdot]}{dt} = 0 = k_1^{Me_3CCl}[(EtO)_2\dot{P}O][Me_3CCl] - 2k_7[Me_3C\cdot]^2 - 2k_{13}[(EtO)_2\dot{P}O][Me_3C\cdot] \tag{12}$$

where $2k_{13}$ refers to the cross-reaction:

$$(EtO)_2\dot{P}O + Me_3C\cdot \rightarrow \text{nonradical products} \tag{13}$$

Equation 12 can be rearranged into the form:

$$\frac{[Me_3CCl]}{[Me_3C\cdot]} = \frac{2k_7[Me_3C\cdot]}{k_1^{Me_3CCl}[(EtO)_2\dot{P}O]} + \frac{2k_{13}}{k_1^{Me_3CCl}} \tag{14}$$

A plot of $[Me_3CCl]/[Me_3C\cdot]$ against $[Me_3C\cdot]/[(EtO)_2\dot{P}O]$ yields a straight line (see Figure 3) from the slope of which $2k_7/k_1^{Me_3CCl}$

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Table III. Relative and Absolute Rate Constants for Some Halogen Atom Abstractions by Diethoxyphosphonyl Radicals at Ambient Temperatures: Comparison with Rate Constants for Analogous Reactions with $Et_3Si\cdot$ and n-$Bu_3Sn\cdot$ Radicals

halide	$k_1/k_1^{Me_3CCl}$	$k_1[(EtO)_2\dot{P}O]$, $M^{-1}\ s^{-1}$	$k_2(Et_3Si\cdot)$,[a] $M^{-1}\ s^{-1}$	$k_3(n\text{-}Bu_3Sn\cdot)$,[b] $M^{-1}\ s^{-1}$
$(CH_3)_3CCl$	(1)	3.7×10^2	2.5×10^6	1.6×10^4
$CH_3(CH_2)_3Br$	27	1.0×10^4	5.4×10^8	1.9×10^7 [c]
$\overline{(CH_2)_4CH}Br$	207	7.7×10^4		2.2×10^7 [d]
$CH_3CH_2CHBrCH_3$	213	7.9×10^4		
$(CH_3)_3CBr$	817	3.0×10^5	1.1×10^9	8.5×10^7
$CH_2=CHCH_2Br$	3180	1.2×10^6	1.5×10^9	
$C_6H_5CH_2Br$	3240	1.2×10^6	2.4×10^9	8.9×10^8 [e]

[a] Reference 10. [b] Reference 11. [c] 1-Bromohexane. [d] Bromocyclohexane. [e] Measured during this work to complete the n-$Bu_3Sn\cdot$ series by competitive reduction of $(CH_3)_3CBr$ and $C_6H_5CH_2Br$ with n-Bu_3SnH followed by VPC analysis for the isobutane and toluene produced.

$= 1.50 \times 10^7$ and from the intercept of which $2k_{13}/k_1^{Me_3CCl} = 2.35 \times 10^6$.

Discussion

The rate constant for the bimolecular self-reaction of *tert*-butyl radicals will be 5.6×10^9 $M^{-1}\ s^{-1}$ under our conditions (see Experimental Section). Combining this value for $2k_7$ with the slope of the plot in Figure 3 yields the absolute rate constant for chlorine atom abstraction from *tert*-butyl chloride, $k_1^{Me_3CCl} = 3.7 \times 10^2$ $M^{-1}\ s^{-1}$. This value has been combined with relative rate constants derived from the data in Table I to obtain the absolute rate constants for halogen abstraction that are listed in Table III. Despite the somewhat roundabout route by which they have been obtained, we believe that these rate constants are probably reliable to within a factor of 2.

For comparative purposes Table III also lists some absolute rate constants for halogen atom abstractions by the triethylsilyl[10] and tri-*n*-butylstannyl[11] radicals at ambient temperatures. As would be expected, the reactivity order for the organic halides is the same toward all three halogen abstracting agents. For any single halide the rate of abstraction decreases in the order $Et_3Si\cdot > n\text{-}Bu_3Sn\cdot > (EtO)_2\dot{P}O$, which no doubt accounts for the infrequent use of diethoxyphosphonyl radicals as halogen atom abstracting reagents.

In their pioneering EPR study of phosphonyl radicals Davies et al.[4] showed that the phosphonyl spectrum could be quenched by a number of simple olefins at low temperatures, its spectrum being replaced by that of an adduct radical, e.g., $(EtO)_2P(O)CH_2\dot{C}Me_2$ with isobutylene. We have found that with several olefins at ambient temperatures (e.g., 1-hexene, cyclopentene, tetramethylethylene) the *tert*-butoxyl radicals abstract allylic hydrogen atoms in preference to the hydrogen from the phosphite. However, this problem did not occur with 2,4,4-trimethylpent-2-ene, and, with 0.032 M of this olefin in our phosphite/peroxide solution, the EPR spectrum of the adduct radical and that of the $(EtO)_2\dot{P}O$ radical could be observed simultaneously. By measuring the absolute radical concentrations at different light intensities (as described above for *tert*-butyl chloride) the rate constant ratios $2k_{16}/k_{15}$ and $2k_{17}/k_{15}$ were determined to be 1.04×10^4 and 6.0×10^4, respectively, for the following three reactions:

$$(EtO)_2\dot{P}O + Me_2C{=}CHCMe_3 \rightarrow (EtO)_2P(O)C(Me)_2\dot{C}HCMe_3 \quad (15)$$

$$2(EtO)_2P(O)C(Me)_2\dot{C}HCMe_3 \rightarrow \text{nonradical products} \quad (16)$$

$$(EtO)_2\dot{P}O + (EtO)_2P(O)C(Me)_2\dot{C}HCMe_3 \rightarrow \text{nonradical products} \quad (17)$$

The rate constant for reaction 16 was measured by the technique of modulated EPR spectroscopy,[34] using the olefin at a concentration of 0.31 M to eliminate the phosphonyl radical. The value obtained for $2k_{16}$ was 1.48×10^9 $M^{-1}\ s^{-1}$, from which $k_{15} = 1.4 \times 10^5$ $M^{-1}\ s^{-1}$ and $2k_{17} = 8.5 \times 10^9$ $M^{-1}\ s^{-1}$, all at room temperature. It is clear that the addition of phosphonyl radicals to olefins, even those which are quite hindered, is a very facile process. Reactions 5 (for which $2k_5 = 3.3 \times 10^9$ $M^{-1}\ s^{-1}$ at 253 K),[19] 13 (for which $2k_{13} = 8.7 \times 10^8$ $M^{-1}\ s^{-1}$ at room temperature), 16, and 17 all occur at rates that are close to diffusion control.

Finally, the EPR competition method using 2,2,4-trimethylpent-2-ene (0.035 M) and benzene (0.29 M) was employed to determine the rate constant for the addition of diethoxyphosphonyl radicals to benzene (reaction 6). A value of 1.4×10^3 $M^{-1}\ s^{-1}$ was obtained for k_6, which is in very satisfactory agreement with the value of 2.9×10^3 $M^{-1}\ s^{-1}$ measured by Griller et al.[20] using a somewhat more direct procedure.

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Registry No. $(EtO)_2P(O)$, 31682-65-2; $(CH_3)_3CCl$, 507-20-0; $CH_3(CH_2)_3Br$, 109-65-9; *cyclo*-$(CH_2)_4CHBr$, 137-43-9; $CH_3CH_2CHBrCH_3$, 78-76-2; $(CH_3)_3CBr$, 507-19-7; $CH_2{=}FcHCH_2Br$, 106-95-6; $C_6H_5CH_2Br$, 100-39-0; $(EtO)_2P(O)H$, 762-04-9; *tert*-BuOOBu-*tert*, 110-05-4; 2,4,4-trimethylpent-2-ene, 107-40-4; benzene, 71-43-2.