(s, 2 H), 5.3-6.2 (m, 4 H); IR (neat) 3000, 2940, 2920, 2850, 1590, 1175, 1140, 1100, 1065, 995, 930, 885, 840, 735, 675, 620 cm^{-1}; MS, *m/e* 307 (M$^+$, 32%), 234 (28) 105 (55), 73 (100); exact mass, *m/e* 307.2138, calcd for $C_{17}H_{33}NSi_2$, *m/e* 307.2151.

1-[Bis(trimethylsilyl)amino]-6-(3,3-dimethoxypropyl)-1,3,5-cycloheptatriene (27c). Yield 36%; a colorless oil; bp 125 °C (0.95 mmHg); ^1H NMR (CCl_4) δ 0.23 (s, 18 H), 2.26 (s, 2 H), 1.55-2.26 (m, 4 H), 3.24 (s, 6 H), 4.31 (t, *J* = 5 Hz, 1 H), 5.40-6.30 (m, 4 H); IR (neat) 3000, 2940, 2880, 2820, 1595, 1505, 1440, 1380, 1175, 1125, 1080, 1070, 1055, 990, 950, 930, 910, 890, 840, 820, 760, 740, 680, 660 cm^{-1}; MS, *m/e* 353 (M$^+$, 3%), 321 (36), 248 (22), 73 (100); exact mass, *m/e* 353.2220, calcd for $C_{18}H_{35}NO_2Si_2$, *m/e* 353.2206.

1-Allyl-6-[bis(trimethylsilyl)amino]-1,3,5-cycloheptatriene (27d). Yield 13%; a colorless oil; bp 110 °C (0.65 mmHg); ^1H NMR (CCl_4) δ 0.10 (s, 18 H), 2.16 (s, 2 H), 2.80 (bd, *J* = 6 Hz, 2 H), 4.65-6.15 (m, 7 H); IR (neat) 3075, 3000, 2950, 2880, 1590, 1550, 1445, 1170, 1130, 990, 960, 930, 910, 880, 840, 820, 755, 740, 700, 680, 620 cm^{-1}; MS *m/e* 291 (M$^+$, 35%), 218 (33) 73 (100); exact mass, *m/e* 291.1860, calcd for $C_{16}H_{29}NSi_2$, *m/e* 291.1838.

Trapping Free Radicals Formed in the Reaction of Ozone with Simple Olefins Using 2,6-Di-*tert*-butyl-4-cresol (BHT)

William A. Pryor,* Jen-tau Gu, and Daniel F. Church

Departments of Chemistry and Biochemistry, Louisiana State University, Baton Rouge, Louisiana 70803

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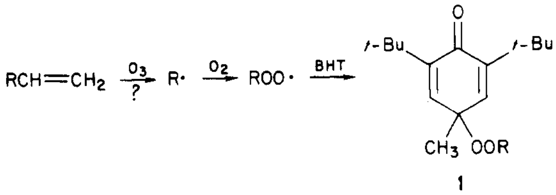
Free radicals are detected from the ozonation of a series of olefins using a BHT trapping technique. We have determined the structure of the adduct when 3,3-dimethylbutene (*tert*-butylethylene) is ozonated at -78 °C and then warmed in the presence of BHT. The adduct can be rationalized as arising from trapping *tert*-butylperoxyl radicals by BHT to give 2,6-di-*tert*-butyl-4-(*tert*-butylperoxy)-4-methyl-2,5-cyclohexadienone (1).

Ozone, one of the most ubiquitous of environmental toxins, causes damage to biological systems both by Criegee ozonolysis (which presumably does not involve free radicals) and by a process that generates free radicals.[1,2] The production of free radicals from ozone/olefin reactions in solution has been somewhat controversial,[3] and it is important to establish unambiguously that free radicals actually are produced. We have used spin trapping techniques to demonstrate radical production,[2a,3] but these data are not entirely satisfactory for two reasons. First, nitrones and nitroso compounds can be converted to nitroxide radicals by processes that do not involve the trapping of free radicals; in other words, ESR spectra of spin adducts can arise by artifactual reactions. Second, spin trapping is difficult to quantify, and we were only able to show that the yield of free radicals from ozone/olefin reactions lies between 0.01 and 10%.[2b] In this communication we report results on the trapping of free radicals from ozone/olefin reactions using BHT as the radical trap. While BHT is not a "spin trap" in the strictest definition of the term, it is a well-known scavenger of oxy radicals, and the structure of the BHT adduct of peroxyl radicals has been elucidated in several cases.[4-7]

We have previously shown that ozone reacts with simple olefins to give peroxyl radicals, and we suggested that these radicals arise from a hydrotrioxide (ROOOH) that is the immediate radical precursor.[2a] One possible mechanism by which olefin/ozone reactions could produce hydrotrioxides is by reaction of ozone at the allylic hydrogen, and we have demonstrated that this type of reaction can occur, using cumene as a model for an olefin with an allylic hydrogen.[8] However, olefins that do not possess allylic hydrogens cannot react by this mechanism; nevertheless, our original study[2] showed that at least one such olefin, 3,3-dimethylbutene (*tert*-butylethylene), gives radicals on reaction with ozone. As a probe of the mechanism in this case, we have studied *tert*-butylethylene by the BHT trapping method. We here present evidence that olefins of the structure RCH=CH_2 or RCH=CMe_2 (where R is *tert*-butyl) react with ozone to give an intermediate that is stable at -78 °C. This intermediate appears to decompose on warming to give alkyl radicals that subsequently react with oxygen to give peroxyl radicals; if BHT is present, these peroxyl radicals are then trapped by BHT to give adducts as shown in eq 1.



1

(1)

Experimental Section

Instrumentation. Proton NMR spectra were recorded with a Varian A-60 NMR spectrometer and both ^1H and ^{13}C NMR spectra with a Bruker WP-200 spectrometer. Mass spectra were obtained on a Hewlett-Packard 5985A mass spectrometer; electron-impact (70 eV) and chemical-ionization (methane) spectra were obtained by a direct-insertion method. Infrared spectra were

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(2) (a) Pryor, W. A.; Prier, D.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 2883-2888. (b) In systems where radicals are generated directly (and cleanly) from initiators, PBN appears to demonstrate a high efficiency in trapping radicals. However, in systems in which peroxyl radicals may be trapped (and where peroxyl spin adducts subsequently rearrange to give alkoxyl spin adducts), the efficiency of spin trapping by PBN appears to be much lower. This describes the spin trapping problem faced with ozone, which appears to produce a mixture of oxy-radicals that are ultimately observed as alkoxyl spin adducts.[2a] We have discussed these aspects of quantitating radical yields by spin trapping, as has E.G. Janzen, K.U. Ingold, and M.V. Merritt and R.A. Johnson (see references cited in reference 2a).

(3) Pryor, W. A.; Prier, D. G.; Church, D. F. *Environ. Res.* **1981**, *24*, 42-52.

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0022-3263/85/1950-0185$01.50/0

Table I. Summary of the Experimental Data on the BHT Adducts of Several Olefins[a,b]

olefin	solvent	flow rate of ozone, μmol/min	ret time of BHT adduct, min	adduct yields,[c,d] mol %
3,3-dimethyl-1-butene	CH_2Cl_2	78–89	5.6	0.14
2,4,4-trimethyl-2-pentene	pentane	104	5.6	0.02
1,2-di-*tert*-butylethylene	pentane	81	5.3	trace
2,4,4-trimethyl-1-pentene	CH_2Cl_2	230	3.9, 6.1[e]	0.12
2-methyl-2-pentene	CH_2Cl_2	115	7.6[f]	0.05
2,3-dimethyl-2-butene	pentane	73	6.6	trace
vinylcyclohexane	pentane	80	6.3	0.07
1-hexene	CH_2Cl_2	163	7.8	0.04
trimethylacetaldehyde	CH_2Cl_2	128	5.7	0.17
n-valeraldehyde	pentane	85	5.2	0.07

[a] Approximately 0.6 molar equiv of ozone were used. [b] HPLC conditions: Partisil 5 ODS-3, solvent CH_3CN/H_2O, 90/10, v/v, flow rate 2.0 mL/min. [c] The yield is calculated as (mol of BHT adduct)/(mol of ozone added). Adduct yields were calculated as the difference between the mol of BHT used and the amount recovered unreacted, as measured by HPLC using an internal standard [2,2-bis(4-(4-(phenylsulfonyl)phenoxy)phenyl)propane]. [d] The adduct yields depend somewhat upon the rate of warming the ozonized olefin plus BHT from −78 °C to room temperature. These yields are not optimized. [e] Two adducts formed in almost equal yields. [f] HPLC flow rate was 1.0 mL/min.

recorded with an IBM Model 32 FT-IR spectrometer. Visible–UV spectra were recorded with a Varian Cary 219 spectrophotometer. The HPLC analysis was accomplished with a Varian Model 5000 with a IBM LC/9540 integrator; the analysis of BHT adducts was on a Partisil 5 ODS-3 reverse phase 30 × 0.4 cm column (Alltech Co.).

Materials. The olefins and most of the solvents were purchased from Aldrich and were used as received unless otherwise specified. Some olefins were purified by simple distillation and column chromatography (Al_2O_3). The BHT was recrystallized from methanol before use.

General Ozonolysis Procedure. Ozone was produced in a Welsbach Model T23 ozone generator and delivered as an ozone/oxygen stream at a rate of 0.1–0.2 mmol of ozone/min.[3] Ozonolysis was carried out to about 60% of the theoretical requirement of the olefin. The amount of ozonation was determined from the amount of olefin remaining after reaction, as determined by NMR. The ozone/oxygen stream was bubbled through a pipet into a solution of the olefin in methylene dichloride or pentane (olefin/solvent generally 1:4, v/v) at −78 °C in a dry ice–acetone bath. Air was then bubbled through for 10–15 s to remove any unreacted ozone.

Isolation of BHT Adduct 1. In a typical experiment, a solution of 3,3-dimethylbutene (3 mL, 2.3 × 10^{-2} mmol) in methylene dichloride (12 mL) was ozonized by the general procedure, and then a BHT solution (0.1 M in CH_2Cl_2, 0.70 mL, 7.0 × 10^{-2} mmol, 0.3 mol % of the ozone used) was added at −78 °C. This solution was allowed to gradually warm to room temperature overnight, the low boiling fraction removed under vacuum, and the residue passed through a silica gel column and eluted with hexane/ether (9:1, v/v) to remove polar components. Only BHT and the BHT adducts were left. These compounds can be separated on a C_{18} reverse-phase TLC plate with a 95% aqueous acetonitrile solution. The second band was scratched out and extracted with ether, the solvent removed under vacuum, and the viscous residue crystallized by adding a small amount of water. Adding larger amounts of BHT, up to 1.2 mol % of the amount of ozone used, did not increase the yield of the BHT adduct. Previous experience with BHT suggests that adding larger excesses of BHT over the radicals to be trapped does not lead to increased trapping efficiency.[7]

Adducts from Ozonolyses of a Mixture of Tetramethylethylene (TME) and Trimethylacetaldehyde. The general ozonolysis procedure was used. An ozone/oxygen stream (73.5 μmol/min, 3.87 mmol) was passed through a mixture of TME (0.921 mL, 7.74 mmol) and trimethylacetaldehyde (0.841 mL, 7.74 mmol) in CH_2Cl_2 (7.0 mL), and then a BHT solution (0.1 M, 0.232 mL in CH_2Cl_2, 0.3% mol % of the ozone used) was added at −78 °C. The initial BHT concentration in the final solution is 2.9 mM. This solution was allowed to warm to room temperature overnight, and the reaction mixture was analyzed by HPLC. Two adducts, 1 and "X", were obtained; X has a retention time matching an adduct obtained from ozonation of TME (see Table I). The yields (based on reacted ozone) of 1 and X were 0.031 and 0.028 mol %, respectively.

Scheme I

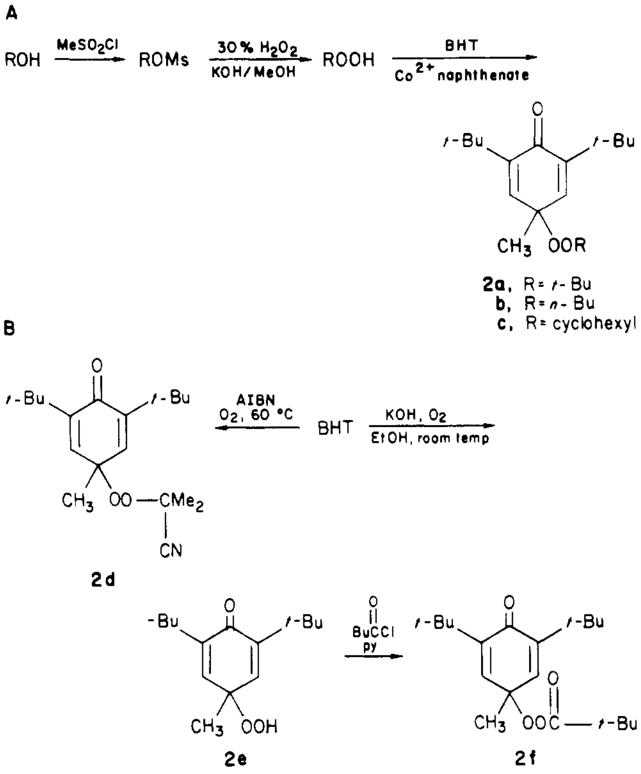
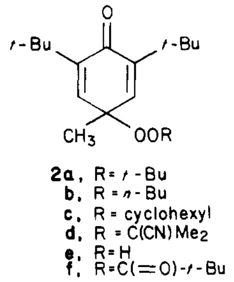


Chart I



Several previously known adducts of BHT and free radicals have been synthesized for comparison to 1. The synthetic routes are shown in Scheme I.

Results

Survey of Olefins. The data in Table I were obtained by using the general ozonolysis procedure (Experimental Section) in which oxygen is present during warmup.

Table II. Summary of Spectral Data of the BHT Adducts

compd	mp, °C	UV (MeOH) λ_{max}, nm	IR (KBr) ν(C=O), cm^{-1}	^{1}H NMR (CDCl$_3$) δ	^{13}C NMR (CDCl$_3$) δ
1		234	1665, 1644	1.18[b] (s), 1.24 (s), 1.33 (s), 6.56 (s)	24.27, 26.51, 29.50, 34.75, 141.8[c]
2a	74	234[d]	1644, 1665	1.18 (s, 9 H), 1.22 (s, 18 H), 1.33 (s, 3 H), 6.55 (s, 2 H)	24.24, 26.49, 29.48, 34.79, 76.17, 79.28, 141.79, 146.69, 186.55
2b	oil	235	1700, 1750	1.23 (s, 18 H), 1.33 (s, 3 H), 0.8–1.7 (m, 7 H), 3.8–4.1 (m, 2 H), 6.54 (s, 2 H)	13.95, 19.44, 24.07, 29.43, 29.85, 34.69, 75.67, 77.61, 140.81, 147.33, 186.2
2c	47–49	235	1700, 1750	1.23 (s, 18 H), 1.32 (s, 3 H), 0.9–2.0 (m, 11 H), 3.6–4.0 (m, 1 H), 6.53 (s, 2 H)	23.89, 25.73, 29.44, 30.46, 34.73, 77.36, 82.66, 140.91, 147.32, 186.52
2d	53	234	1664	1.25 (s, 18 H), 1.40 (s, 3 H), 1.55 (s, 6 H), 6.58 (s, 2 H)	23.87, 24.92, 29.43, 34.84, 75.00, 78.28, 120.4, 140.1, 148.0, 186.3
2e	105–109	235	1669, 1647	1.21 (s, 18 H), 1.40 (s, 3 H), 2.02 (s, 1 H), 6.53 (s, 2 H)	28.1, 29.4, 34.5, 67.4, 143.3, 145.3, 186.1

[a] Proton NMR spectra, Varian A-60; ^{13}C NMR spectra, Bruker WP-200; IR spectra, Perkin-Elmer 237B and IBM IR/32 FT-IR; UV spectra, Varian Cary 219. [b] Because of impurities in 1a, integrals are not shown. [c] Some peaks are missing compared with 2a due to weakness of the spectrum. [d] log E = 4.04.

Table III. Summary of Mass Spectral Data (by Electron Impact) of the BHT Adducts

comp	mass spectra (direct insertion), m/e
1	234, 219, 164, 163, 161, 149, 135, 119, 57
2a	234, 219, 205, 163, 161, 149, 135, 119, 57
2b	234, 219, 164, 163, 161, 149, 135, 119, 57
2c	234, 219, 164, 163, 161, 149, 119, 57
2d	234, 219, 164, 163, 161, 149, 135, 119, 91, 57
2e	279, 221, 193, 180, 179, 165, 151, 137, 123, 91, 57

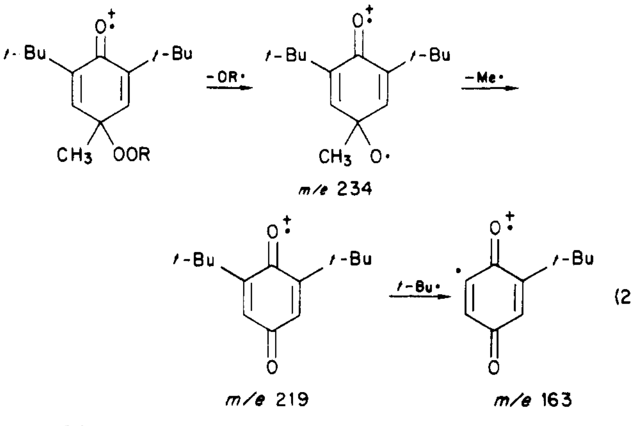
Table IV. Summary of Mass Spectral Data (by Chemical Ionization) of the BHT Adducts[a]

comp	mass, m/e (relative intensity)		
	$(M + H)^+$	$(M + C_2H_5)^+$	$(M + C_3H_5)^+$
1	309 (35.3)	337 (5.2)	349 (7.3)
2a	309 (31.0)	337 (3.9)	349 (5.6)
2b	309 (15.3)	337 (3.6)	349 (3.1)
2c	335 (15.3)	363 (2.2)	375 (2.1)
2d	320 (23.0)	348 (1.9)	360 (0.2)

[a] Chemical ionization using methane as carrier gas; by direct insertion.

(Chart I shows the structures of the adducts studied here.) In this method, unstable species decay to radicals that react with oxygen and only alkylperoxyl radical adducts of BHT are observed.[6] A single adduct was obtained from ozonated 3,3-dimethylbutene, and it was subjected to a more thorough study.

Adduct Structure. The BHT adduct of ozonated 3,3-dimethylbutene, **1**, was isolated to obtain its UV, FT-IR, ^{1}H and ^{13}C NMR, and mass spectra. The UV spectrum exhibited a maximum absorption at 234 nm, in agreement with a peroxyquinone structure[4,6] (Table II). The FT-IR spectrum was obtained, and the peroxyquinone region (1740–834 cm^{-1}) shows the same absorption pattern as do known compounds[4] (Table I). The 834–1740 cm^{-1} region for **1** and **2a** are virtually identical (shown as Figure 1 in the supplementary material; see the paragraph at the end of the paper). The electron-impact mass spectrum indicates an alkylperoxyquinone structure (Table III), as illustrated in eq 2, where m/e ratios marked were observed in the MS spectrum (m/e 234, 219, and 163).



(2)

Table IV shows the mass spectrum of **1** and **2a** obtained by chemical ionization. The parent molecular weight of **1** can be seen to be identical with that of **2a**, identifying the fragment added to BHT as C_4H_9OO–.

Table II gives absorbances for both proton and ^{13}C spectra for all the adducts. The proton NMR spectra rule out structures in which the trapped radical has the structure RCH_2OO– or R_2CHOO–, since the protons adjacent to the peroxyl bond would give absorbances in the region 3.4–4.1 ppm, a region that is clean in **1** (and also the known **2a**). The proton NMR spectra of **1** and **2a** are compared in Figure 2 and their ^{13}C NMR spectra are

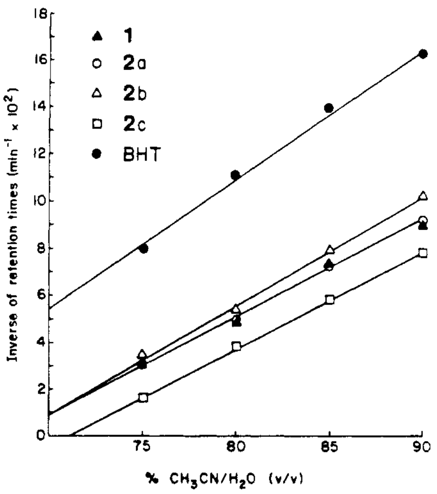


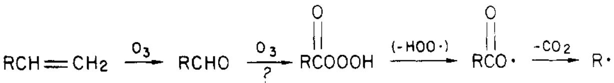
Figure 4. The plot of $1/t$ vs. the solvent ratio of CH_3CN/H_2O (Partisil 5 ODS-3, 30 × 0.4 cm; flow rate 1.0 mL/min).

compared in Figure 3 in the supplementary material.

The retention time (t) in reverse phase (HPLC) is related to the nature of the R group. Figure 4 shows that a plot of $1/t$ vs. the solvent ratio (CH_3CN/H_2O), and the lines for **1** and the *tert*-butylperoxyl adduct (**2a**) overlap, suggesting that the major BHT adduct of ozonated 3,3-dimethylbutene is **2a**. Figure 4 shows that the other synthetic quinones chromatograph differently than does **1** or **2a**.

Discussion

Our data suggest that *tert*-butylethylene undergoes ozonation to give small yields of *tert*-butyl radicals, which react with oxygen to ultimately give *tert*-butylperoxyl radicals that are trapped by BHT. The mechanism responsible for producing the *tert*-butyl radicals is not obvious. As is shown in Table I, the aldehyde RCHO gives a yield of adduct **1** that is approximately equal to that obtained from $RCH{=}CH_2$, where R is the *tert*-butyl group. Thus, one possible mechanism, shown in eq 3, is that the olefin undergoes Criegee ozonation to give the aldehyde, which undergoes further ozonation, ultimately to give R· radicals.[9-11]



$$\mathrm{RCH{=}CH_2} \xrightarrow{O_3} \mathrm{RCHO} \xrightarrow[?]{O_3} \mathrm{R\overset{O}{\overset{\|}{C}}OOOH} \xrightarrow{(\text{-HOO}\cdot)} \mathrm{R\overset{O}{\overset{\|}{C}}O\cdot} \xrightarrow{-CO_2} \mathrm{R\cdot} \quad (3)$$

Equation 3 shows the acyl hydrotrioxide undergoing scission in the thermochemically preferred[2,8] manner to give HOO· and acyloxyl radicals, rather than HO· and acylperoxyl radicals. Despite the fact that this mode of scission to form HOO· is thermochemically preferred, White and Bailey[11] suggested that the aroyl hydrotrioxide produced in the ozonation of benzaldehyde decomposes by splitting out an HO· radical. To probe this point, we examined the gas in the head space above the solutions produced by ozonation of *tert*-butylethylene. At short reaction times, the gas consisted of CO_2, not CO, supporting the formulation shown in eq 3. If RC(=O)OOOH were produced and underwent homolysis to form RC(=O)OO·, loss of oxygen and CO might be expected.

Table V. The Second-Order Rate Constants for the Reactions of Ozone with Olefins in CCl_4 Solutions at Room Temperature

olefin	k, M^{-1} s^{-1}	log A/s	E_a, kcal/mol	ref
tetramethylethylene	200 000			*a*
3,3-dimethylbutene	27 500	6.4	2.6	*b*
trimethylacetaldehyde	107	8.3	8.6	*b*

[a] Williamson, D. F.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 4248–4252, 3668–3672. [b] Pryor, W. A.; Giamalva, D., unpublished results.

Furthermore, BHT trapping of the RC(=O)OO· radical should lead to adduct **2f**, an adduct[4,5,12,13] that we prepared by the route shown in Scheme I. Adduct **2f** clearly is not identical with adduct **1**; for example, **2f** elutes very much faster than does **1** using HPLC and gives a different proton NMR spectrum.

The mechanism shown in eq 3, while reasonable at first glance, has problems. First, we have measured the rates of reaction of olefins and RCHO with ozone at 25 °C using a stopped-flow technique. (See Table V.) As can be seen, olefins are very much more reactive than are aldehydes toward ozone even at 25 °C, and it might be expected that ozone would not react with an aldehyde, especially at −78 °C, in the presence of unreacted olefin. However, as described in the Experimental Section, we find that an equimolar mixture of tetramethylethylene (TME) and pivaldehyde reacts with slightly less than 0.5 molar equiv of ozone to give two adducts, one the adduct that is formed from TME alone and the other equivalent to compound **1**. Thus, some unknown complexity causes this aldehyde to react even in the presence of olefin, despite the rate constants obtained for individual experiments shown in Table V. It is possible that the ozone/air mixture, which enters the reaction mixture at room temperature (rather than −78 °C) and liberates considerable heat on reaction, reacts in a hot microenvironment and displays less selectivity than would be expected at −78 °C. Another possibility is that some intermediate[14] formed from the ozone/olefin reaction reacts with the aldehyde, rather than ozone itself. Still a third possibility is that ozone (or a species such as the oligomer[15] from the ozone/olefin reaction) induces a chain autoxidation of the aldehyde, and ozone itself does not react directly with the aldehyde.[16]

More complex mechanisms could be written to rationalize the production of R· radicals from the olefin $RCH{=}CH_2$. However, this study was not designed to test such mechanisms; thus, at present, it seems most conservative to postulate eq 3 as the source of the R· radicals and to explain the unexpected reactivity of aldehydes in the presence of olefins in terms of one of the factors suggested above.

The yields of trapped radicals using BHT (shown in Table I) can be compared with those obtained by using

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(16) An interesting observation is that 1,2-di-*tert*-butylethylene, which is ozonized to give only small amounts of RCHO,[17] gives only a trace of adduct 1. This olefin has been reported by Ramachandran and Murray to give no detectable radicals by ESR upon ozonation.[17]

(17) Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2197–2201.

the nitrone spin trap PBN.[2a] For example, *tert*-butylethylene gives a radical yield of 0.1% using the BHT method; PBN gives a radical yield of 0.004% with this olefin, confirming our suggestion[2a] that PBN traps radicals with about 1% efficiency in these ozone systems.[2b]

This work demonstrates the usefulness of BHT as a "spin trap". Carbon-centered radicals can be converted to peroxyl radicals in the presence of oxygen, and BHT traps these radicals with high efficiency. The use of BHT in place of a nitrone spin trap clearly conveys some advantages: BHT yields a stable, diamagnetic species that can be quantified by normal chromatographic methods, rather than by ESR. While the identification of the radical that is trapped by BHT using GC/MS is not trivial, our data do show that this identification can be made (at least for simple R groups) using GC/MS in collaboration with NMR.

Acknowledgment. This work was supported in part by grants from the National Science Foundation, the National Institutes of Health (HL-16029), and a Contract from the National Foundation for Cancer Research.

Supplementary Material Available: Figure 1, IR spectra, Figure 2, ^1H NMR spectra, and Figure 3, ^{13}C NMR spectra of compounds 1 and **2a** (3 pages). Ordering information is given on any current masthead page.

Triphenylborane Methanolysis and Equilibrium Association between Triphenylborane or Diphenylborinate Esters and Alcohols

P. J. Domaille, J. D. Druliner,* L. W. Gosser, J. M. Read, Jr., E. R. Schmelzer, and W. R. Stevens

Central Research & Development, Engineering and Petrochemicals Departments, E. I. du Pont de Nemours & Co., Wilmington, Delaware 19898

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Treatment of triphenylborane (TPB) with simple alcohols (ROH) results in varying extents of TPB(ROH)$_n$ complex formation. Equilibrium formation constants strongly depend on steric bulk of the alcohol and range from about 300 for methanol where $n = 3$ to zero for *tert*-butyl alcohol. Steric effects are also important in the ester exchange reaction: $R^1OH + Ph_2BOR \rightleftharpoons ROH + Ph_2BOR^1$. Alcoholysis of TPB to give Ph_2BOR + benzene is catalyzed by acids, bases, and certain metals and is inhibited by excess alcohol. The rates of methanolysis of TPB were measured by ^1H NMR and IR at room temperature for different TPB/methanol ratios and the kinetics modeled by computer. The rate is first order in TPB and zero order in methanol.

Two aspects of triarylborane chemistry have received considerable study: association of such boranes with a variety of bases and protonolysis of the B–C bond.[1,2] Bases which undergo complexation with triarylboranes include hydroxide, alkoxide, cyanide, amines, and nitriles.[3] Steric effects strongly affect complex formation strengths as first delineated by brown and co-workers in their studies of steric strain in trialkylborane/amine complexes.[4] Little has been reported about equilibrium association between triarylboranes and alcohols, perhaps owing to the weakness of such interactions and to the fact that simple alcohols in nonpolar solvents exist largely as mixtures of dimers, trimers, tetramers, ...*n*-mers, thus adding analytical complexisy.[5] The B–C bond of triaryl- or trialkylboranes can undergo protonolysis but generally requires catalysis by acids or bases. For example, pure trialkylboranes are remarkably stable toward hydrolysis.[6] Likewise, $PhB(OH)_2$ underwent only 0.07% methanolysis when heated at reflux for 6 days in methanol.[7] This paper summarizes a study of methanolysis of triphenylborane (TPB) and includes a kinetic model which takes into consideration equilibria for MeOH self-association and complexation between TPB and MeOH. It is concluded that the rate of $Ph_2B(OMe)$ formation is first order in TPB and zero order in MeOH concentrations, when catalyzed by carboxylic acids or certain active metals.

Table I. ^{11}B NMR Chemical Shifts for TPB and Its Reaction Products and Equilibrium Association Complexes with Methanol in Freon-11 at 25 °C

compd	^{11}B chem shift[a]	ref
TPB	+68.0	
$Ph_2B(MeO)$	+45.7	
TPB(MeOH)$_n$	+39.0	
$PhB(OMe)_2$	+29.0	
$Ph_2B(OEt)$	+45.1	8
$PhB(OMe)_2$	+28.6	9
$PhB(OEt)_2$	+28.6	10
$B(OMe)_3$	+18.2	11
$B(OEt)_3$	+17.6	12

[a] Chemical shifts are referenced to $BF_3{\cdot}Et_2O$ with positive values to higher frequencies.

Reversible Complex Formation

TPB complexes reversibly with alcohols, the stabilities of the TPB(ROH)$_n$ complexes varying inversely with increasing steric size of the alcohol (eq 1). Evidence for

$$\mathrm{TPB} + n\text{-}\mathrm{ROH} \rightleftharpoons \mathrm{TPB(ROH)}_n \qquad (1)$$

formation of TPB(ROH)$_n$ complexes was obtained from IR, ^{11}B, ^{13}C, and ^1H NMR, and UV spectra. A CCl_4 solution containing 0.5 M amounts of TPB and methanol

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