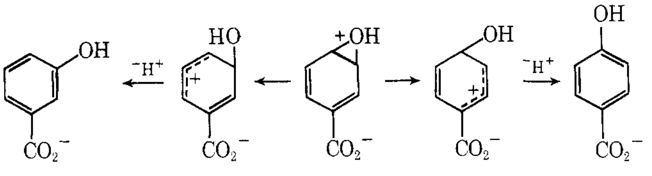
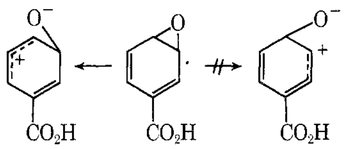
opens to form an incipient carbonium ion at the 1 or 2 position, both would be allylically stabilized by the adjacent double bond (eq 5). On the other hand, the protonated carboxyl is strongly electron withdrawing ($\sigma^+ = +0.42$). This effect should be particularly significant on the π electrons of the double bond between carbons 3 and 4. As a result, these electrons would not be as available for stabilization of a positive charge as would the electrons in the π bond between carbons 5 and 6. Consequently, the opening which leads to formation of the meta isomer would be of lower energy than the opening which leads to the *p*-hydroxybenzoic acid, as shown in eq 6.

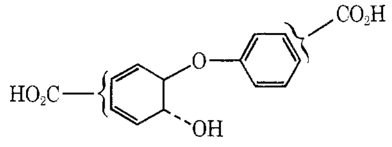


(5)



(6)

In an effort to correlate the reaction of I with the reaction of previously studied arene oxides, the rate of aromatization of I was measured in 50% dioxane-water. At high pH the reaction was first order. Although the observed rate constant was smaller than that predicted from the $\sigma^+\rho$ plot, the agreement was not unreasonable. At pH 0.5, the reaction exhibited biphasic kinetics. This was possibly due to some type of nucleophilic participation by the dioxane oxygens. In conjunction with this, it was found that I also undergoes some sort of transformation on standing in THF. The reaction probably involves rearrangement of 1 to a mixture of *m*- and *p*-hydroxybenzoic acid that undergoes nucleophilic addition to 1 to afford a mixture of products (5). The transformation is analogous to the formation of *trans*-6-phenoxycyclohexa-2,4-dien-1-ol from oxepin-benzene oxide.[14]



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Acknowledgment. This work was supported by a National Institutes of Health grant to Thomas C. Bruice.

Registry No.—1, 51380-68-8; 2, 51380-69-9; 3, 51380-70-2; 4, 51380-71-3; 2,5-dihydroxybenzoic acid, 490-79-9.

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Electron Spin Resonance Studies of Hydrogen Transfer to Alkoxy Radicals from the Hydroxyl Group of Alcohols

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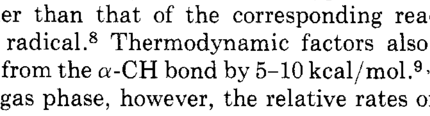
The esr spectra of *tert*-butyl radicals are observed during the reactions of various alkoxy radicals with tertiary alcohols containing one or more *tert*-butyl groups. The homolytic fragmentation of the alcohol is attributed to hydrogen transfer from the hydroxylic function to the alkoxy radical. Structural factors pertinent to the alcohol and alkoxy radical are explored in hydrogen transfer reactions of the hydroxyl group. Hydrogen bonding of alcohols to HF strongly inhibits the transfer of hydrogen from a hydroxylic function.

In solution, the majority of alcohols are preferentially attacked by free radicals at the α-CH bond, with the exception of tertiary alcohols, of course. The resulting α-hydroxyalkyl radicals have been trapped by olefins and their electron spin resonance spectra examined.[1-4]

Abstraction of the hydroxylic proton has been less commonly observed. For example, deuterium-labeling studies indicate that methanol reacts with methyl radicals in solution at the carbon-hydrogen bond 15 times faster than at the hydroxylic position at 30°.[5-7] The activation energy for hydrogen abstraction by methyl radical has been estimated to be 8.4 kcal/mol, which is approximately 3 kcal/mol higher than that of the corresponding reaction with methoxy radical.[8] Thermodynamic factors also favor abstraction from the α-CH bond by 5-10 kcal/mol.[9,10]



$$CH_3\cdot + CH_3OH \longrightarrow \dot{C}H_2OH + CH_4 \quad (1)$$
$$CH_3\cdot + CH_3OH \longrightarrow CH_3O\cdot + CH_4 \quad (2)$$

In the gas phase, however, the relative rates of reactions 1 and 2 are reversed, and the O-H bond is preferentially broken. Solvent effects on the reactions of hydroxyl groups and free radicals could be partly accounted for by the differences in hydrogen bonding in the initial and final states.[11,12] Methoxy radical has been established as the most abundant species produced in the γ-radiolysis of liquid methanol.[13,14]

$$CH_3OH \longrightarrow CH_3O\cdot + H\cdot$$

The competition between the removal of a hydrogen from an α carbon or oxygen is not readily ascertained. Thus, the esr spectra of alkoxy radicals, unlike those of alkyl radicals, are broadened beyond detection in solution, and this direct technique is not an adequate probe for detecting these oxygen-centered radicals in solution.[15] Chemical and spin traps have been used for alkoxy radicals derived from various alkyl peroxides and other precursors except alcohols.[16-18]

In the course of our investigations of oxygen-substituted alkyl radicals from tertiary alcohols,[19] we unexpectedly observed the esr spectra of alkyl radicals derived from the fragmentation of the alcohol, *e.g.*

$$(CH_3)_3CC(CH_3)_2OH + RO\cdot \nrightarrow (CH_3)_3C\cdot$$

The results are most readily accommodated by postulating the ready formation and subsequent β-scission of an alkoxy radical intermediate according to eq 3 and 4.

$$(CH_3)_3CC(CH_3)_2OH + RO\cdot \longrightarrow (CH_3)_3CC(CH_3)O\cdot + ROH \quad (3)$$

$$(CH_3)_3CC(CH_3)_2O\cdot \longrightarrow (CH_3)_3C\cdot + (CH_3)_2CO \quad (4)$$

In this paper we wish to present our study of the homolytic transfer of hydrogen from alcohols. After this work was largely completed, Griller and Ingold reported similar results.[20]

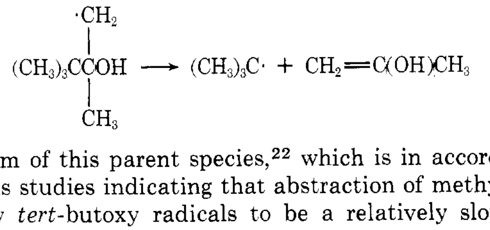
Results and Discussion

The photolysis of di-*tert*-butyl peroxide (DTBP) with ultraviolet radiation constitutes a useful technique for the generation of *tert*-butoxy radicals in solution for a variety of esr studies.[21]

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \quad (5)$$

$$Bu^tO\cdot + RH \longrightarrow Bu^tOH + R\cdot \quad (6)$$

Hydrogen Transfer from tert-Butylcarbinols. The intense esr spectrum of the *tert*-butyl radical shown in Figure 1 with resolved second-order splittings was obtained when a cyclopropane solution of DTBP and *tert*-butyldimethylcarbinol (triptyl alcohol) was irradiated in the cavity of the esr spectrometer. The spectrum appeared immediately upon irradiation of the solution and was essentially unchanged between −140 and −30°. The same spectrum was also observed when *tert*-butyldimethylcarbinol was treated with dicumyl peroxide, which shows unequivocally that the *tert*-butyl radical was derived from the carbinol. Furthermore, the esr spectrum of the *tert*-butyl radical was derived from a variety of tertiary carbinols containing one or more α-*tert*-butyl substituents as listed in Table I, including tri-*tert*-butylcarbinol, which has no β hydrogen. The latter precludes the possibility of the cleavage proceeding *via* a carbon-centered species such as that in eq 7. Furthermore, we did not observe the esr



$$(CH_3)_3C\overset{\cdot CH_2}{\underset{CH_3}{C}}OH \longrightarrow (CH_3)_3C\cdot + CH_2{=}C(OH)CH_3 \quad (7)$$

spectrum of this parent species,[22] which is in accord with previous studies indicating that abstraction of methyl protons by *tert*-butoxy radicals to be a relatively slow and unimportant process.[21] The spectrum in Figure 1, how-

Table I
Reactions of Alkoxy Radicals with *tert*-Butylcarbinols

Alcohol $R^1R^2R^3COH$								
R^1	R^2	R^3	Registry no.	Alkoxy[a] radical	Registry no.	Radical observed	Registry no.	Hyperfine splitting,[b] G
CH_3	CH_3	$(CH_3)_3C$	594-83-2	$Bu^tO\cdot$	3141-58-0	$(CH_3)_3C\cdot$	1605-73-8	$a_H = 22.73$[c]
CH_3	CH_3	$(CH_3)_3C$		$PhC(CH_3)_2O\cdot$	16812-36-5	$(CH_3)_3C\cdot$		
CH_3	CH_3	$(CH_3)_3C$		$CF_3O\cdot$	21811-29-0	$\Delta\cdot$[e]		$a_\alpha = 6.69$, $a_\beta = 23.47$
						$FCH_2CH_2CH_2\cdot$	38816-77-2	$a_\alpha = 22.52$, $a_\beta = 27.97$
CH_3	$(CH_3)_2CH$	$(CH_3)_3C$	29772-39-2	$Bu^tO\cdot$		$(CH_3)_3C\cdot$		$a_H = 22.70$
CH_3	$(CH_3)_2CH$	$(CH_3)_3C$		$CF_3O\cdot$		$(CH_3)_2\dot{C}C(CH_3)(Bu^t)OH$	51392-63-3	Not observed
CH_3	$(CH_3)_3C$	$(CH_3)_3C$	5857-69-2	$Bu^tO\cdot$		$(CH_3)_3C\cdot$		$a_H = 22.76$
						$\cdot CH_2C(Bu^t)_2OH$	51392-64-4	Not observed
CH_3CH_2	$(CH_3)_3C$	$(CH_3)_3C$	32579-68-3	$Bu^tO\cdot$		$(CH_3)_3C\cdot$, broad singlet[d]		$a_H = 22.68$
$(CH_3)_2CH$	$(CH_3)_3C$	$(CH_3)_3C$	5457-42-1	$Bu^tO\cdot$		$(CH_3)_3C\cdot$		$a_H = 22.74$
						$(CH_3)_2CC(Bu^t)_2OH$, broad singlet	51392-65-5	Not observed
$(CH_3)_2CH$	$(CH_3)_3C$	$(CH_3)_3C$		$CF_3O\cdot$		$\Delta\cdot$, $FCH_2CH_2CH_2\cdot$		
CH_3	C_6H_5	$(CH_3)_3C$	21811-48-3	$Bu^tO\cdot$		$(CH_3)_3C\cdot$		$a_H = 22.73$
$(CH_3)_3C$	$(CH_3)_3C$	$(CH_3)_3C$	41902-42-5	$Bu^tO\cdot$		$(CH_3)_3C\cdot$		$a_H = 22.79$
						$\Delta\cdot$, broad singlet		
$(CH_3)_3C$	$(CH_3)_3C$	$(CH_3)_3C$		$CF_3O\cdot$		$\Delta\cdot$		

[a] $Bu^tO\cdot$ from DTBP, $CF_3O\cdot$ from bis(trifluoromethyl) peroxide in cyclopropane solutions. [b] Measured at −80°. [c] $g = 2.00276$. [d] In addition to a 1:2:1 triplet with splitting of 21.95 G, $g = 2.00274$. [e] Cyclopropyl radical.

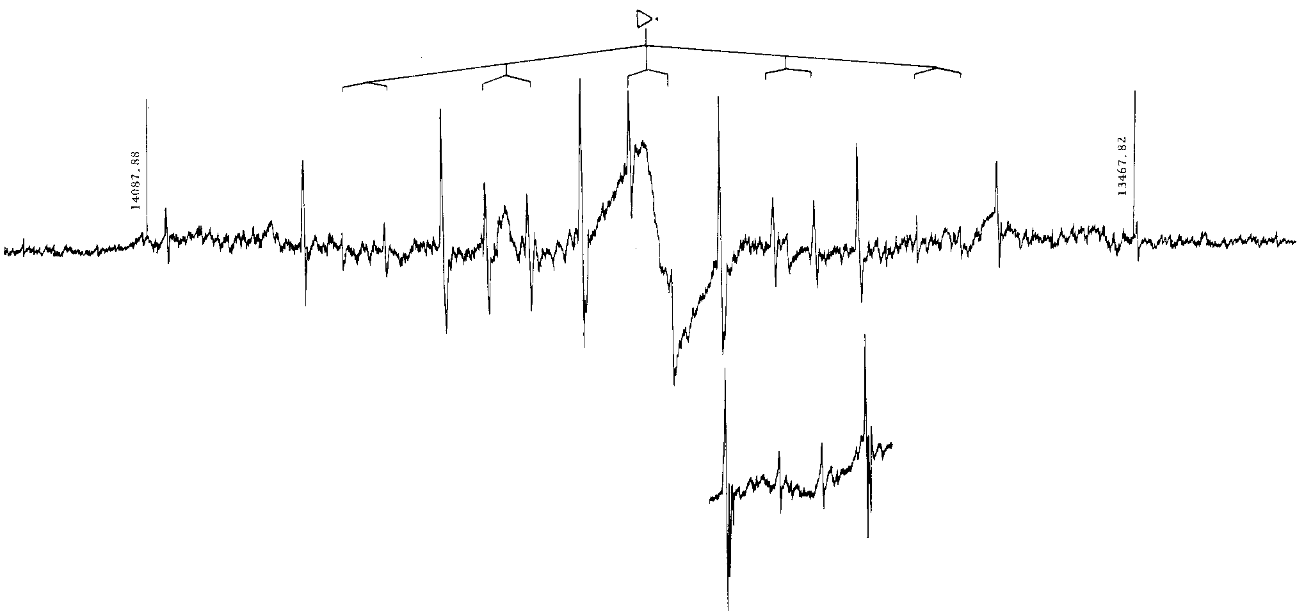
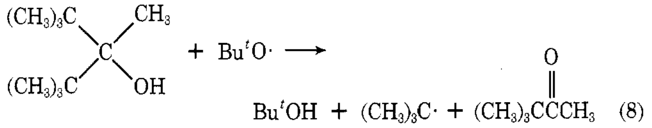


Figure 1. Esr spectrum of the *tert*-butyl radical and the cyclopropyl radical from the reaction of *tert*-butyldimethylcarbinol with *tert*-butoxy radical in cyclopropane solution. Inset below shows resolved second-order splittings for part of the spectrum of *tert*-butyl radical. Proton nmr field markers are in kilohertz.

ever, does show the presence of cyclopropyl radicals derived from the solvent, in addition to an unidentified broad absorption centered at $\langle g \rangle = 2.0028$, which we have been unable to resolve further. The products of the photolysis under these conditions were not examined quantitatively. However, qualitative analysis indicated that significant amounts of pinacolone and *tert*-butyl alcohol are derived from di-*tert*-butylmethylcarbinol, which is consistent with the process described in reaction 8.



$$\mathrm{((CH_3)_3C)_2C(CH_3)OH + Bu^tO\cdot \longrightarrow Bu^tOH + (CH_3)_3C\cdot + (CH_3)_3C\overset{O}{\overset{\|}{C}}CH_3} \quad (8)$$

Abstraction of hydrogen from alcohols was also examined with other oxygen-centered radicals. With *tert*-amyloxy radicals derived from di-*tert*-amyl peroxide, the rate of β-scission was apparently too fast to compete with hydrogen abstraction, and only the esr spectrum of the ethyl radical was observed in the presence of triptyl alcohol. Independent studies have shown that reaction 9 is roughly

$$\mathrm{CH_3CH_2C(CH_3)_2O\cdot \longrightarrow CH_3CH_2\cdot + (CH_3)_2CO} \quad (9)$$

300 times faster than the cleavage of *tert*-butoxy radical and has an activation energy that is smaller by at least 10 kcal/mol.[23] Diisopropyl peroxide under the same conditions afforded only the spectrum of α-hydroxyisopropyl radical, which is derived from isopropyl alcohol produced during the rapid induced decomposition of the peroxide,[24] *e.g.*

$$\mathrm{(CH_3)_2CHO\cdot + (CH_3)_2CHOOCH(CH_3)_2 \longrightarrow (CH_3)_2CHOH + (CH_3)_2CHOO\dot{C}(CH_3)_2} \quad (10)$$

$$\mathrm{(CH_3)_2CHOO\dot{C}(CH_3)_2 \longrightarrow (CH_3)_2CO + (CH_3)_2CHO\cdot}$$

$$\mathrm{(CH_3)_2CHO\cdot + (CH_3)_2CHOH \longrightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH}$$

Hydrogen peroxide (90%) was too insoluble in the hydrocarbon medium to be useful.

If polar effects in the transition state for hydrogen abstraction are considered, the rate should be enhanced by electronegative species such as trifluoromethoxy radicals owing to the participation of structures such as Ib. Con-

$$\mathrm{RO\cdot + R'OH \longrightarrow [\underset{Ia}{RO\cdot H{-}OR'} \longleftrightarrow \underset{Ib}{RO^-H^+OR'}]^* \longrightarrow products} \quad (11)$$

sidering this possibility, we were disappointed to find that photolysis of solutions of bis(trifluoromethyl) peroxide and *tert*-butylcarbinols afforded only the esr spectrum of the solvent-derived radicals, *i.e.*, cyclopropyl and γ-fluoropropyl. The latter is presumably derived from fluorine atom *via* fragmentation of the intermediate trifluoromethoxy radical followed by ring opening of cyclopropane. We interpret the lack of attack on alcohol under these conditions to the strong hydrogen-bonding properties of hydrogen fluoride liberated during the spontaneous decomposition of trifluoromethanol. Deactivation of the alcohol can be shown independently by the deliberate addition of anhydrous hydrogen fluoride to a pentane solution of triptyl alcohol and DTBP. Subsequent photolysis of the mixture afforded only the esr spectrum of the solvent-derived radical.

$$\mathrm{CF_3O\cdot + ROH \longrightarrow CF_3OH + R\cdot} \quad (12)$$

$$\mathrm{CF_3OH \xrightarrow{fast} F_2CO + HF}$$

$$\mathrm{ROH + HF \longrightarrow ROH\cdots F\cdots H}$$

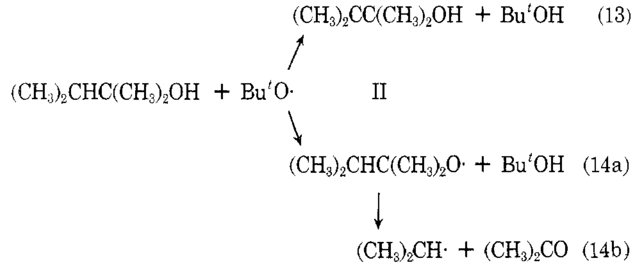
Structural Effects of the Alcohol in Hydrogen Transfer. A variety of other alcohols listed in Table II were also examined in the presence of DTBP under similar conditions. In accord with previous studies, methyl alcohol afforded the esr spectrum of the hydroxymethyl radical and the spectrum of α-hydroxyisopropyl radical was observed with isopropyl alcohol. No resolvable spectrum was obtained from *tert*-butyl alcohol with the use of either *tert*-butoxy or trifluoromethoxy radical as the abstracting agent. The absence of the spectrum of β,β-dimethyl-β-hydroxyethyl radical is in accord with the general inertness of methyl protons under these conditions (*vide supra*).

A number of simultaneous processes can be observed with isopropyldimethylcarbinol. Thus, this alcohol in the presence of *tert*-butoxy radical affords the spectrum of isopropyl radical in addition to that of the alcohol-derived radical II in eq 13. In the latter regard it is interesting to

Table II
Reactions of Alcohols with Alkoxy Radicals

Alcohol R¹R²R³COH R^1	R^2	R^3	Registry no.	Alkoxy radical[a]	Radical observed	Registry no.	Hyperfine splitting, G	⟨g⟩
H	H	H	67-56-1	$Bu^tO\cdot$	$HOCH_2\cdot$	2597-43-5	$a_{CH_2} = 17.95$ $a_{OH} = 1.63$	2.00327
H	H	H		$CF_3O\cdot$	$HOCH_2\cdot$			
H	CH_3	CH_3	67-63-0	$Bu^tO\cdot$	$HO\dot{C}(CH_3)_2$	5131-95-3	$a_{CH_3} = 19.35$ $a_{OH} = 0.93$	2.00316
H	CH_3	CH_3		$CF_3O\cdot$	$HO\dot{C}(CH_3)_2$			
CH_3	CH_3	CH_3	75-65-0	$Bu^tO\cdot$	$CH_3\cdot$	2229-07-4	Not observed	
CH_3	CH_3	CH_3		$CF_3O\cdot$	$HO(CH_3)_2CCH_2\cdot$	5723-74-0	Not observed	
CH_3	CH_3	$(CH_3)_2CH$	594-60-5	$Bu^tO\cdot$	$(CH_3)_2CH\cdot$	2025-55-0	$a_\alpha = 21.87$ $a_\beta = 24.60$	2.00268
					$HO(CH_3)_2C\dot{C}(CH_3)_2$	51392-66-6	$a_{CH_2} = 22.63$	2.00268
CH_3	CH_3	$(CH_3)_2CH$		$CF_3O\cdot$	$\Delta\cdot$, $FCH_2CH_2CH_2\cdot$			

[a] Bu^tO from DTBP, $CF_3O\cdot$ from bis(trifluoromethyl) peroxide in cyclopropane solutions. [b] Measured at −80°.



$(CH_3)_2\dot{C}C(CH_3)_2OH + Bu^tOH$ (13)

$(CH_3)_2CHC(CH_3)_2OH + Bu^tO\cdot$ II

$(CH_3)_2CHC(CH_3)_2O\cdot + Bu^tOH$ (14a)

$(CH_3)_2CH\cdot + (CH_3)_2CO$ (14b)

note that the *tert*-butylcarbinols in Table I containing more highly congested isopropyl groups did not afford esr spectra of analogous species. Variation of the temperature between −140 and −40° during photolysis did not appreciably alter the intensity of the esr spectrum of isopropyl radical relative to that of II.

Abstraction of hydrogen from the side chain appears to be a dominant process with other tertiary alkyldimethylcarbinols we examined. Thus, the benzyl-, alkyl-, and cyclopropyldimethylcarbinols on similar treatment afforded no spectrum of the alkyl radical resulting from fragmentation of the alcohol. Instead, only the spectra of the radicals derived by reactions at the alkyl groups were present, but their structures were not examined further.

Rates and Intermediates in Hydrogen Transfer from Alcohols. The simultaneous observation of the esr spectra of cyclopropyl and *tert*-butyl radicals during the photolysis of a cyclopropane solution of tri-*tert*-butylcarbinol and DTBP suggests that the rate of hydrogen transfer from the alcohol may be based on the following competitive scheme

$$Bu^tO\cdot + ROH \xrightarrow{k_1} RO\cdot + Bu^tOH \quad (15)$$

$$Bu^tO\cdot + SH \xrightarrow{k_2} S\cdot + Bu^tOH \quad (16)$$

$$RO\cdot + SH \xrightarrow{k_3} S\cdot + ROH \quad (17)$$

$$RO\cdot \xrightarrow{k_4} B\cdot + (CH_3)_2CO \quad (18)$$

$$S\cdot, B\cdot + \Sigma\chi_i \xrightarrow{k_5} \text{nonradical products} \quad (19)$$

where S· and B· represent cyclopropyl and *tert*-butyl radicals, respectively. The bimolecular rate constants k_5 are assumed to be the same for S· and B· and to include only interactions with other radical species $\Sigma\chi_i$ extant in solution. Under these simplifying conditions the steady-state concentrations of S· and B· are given by eq 20, if $k_2 \approx k_3$.

$$\frac{[S\cdot]}{[B\cdot]} = \frac{k_2[SH]}{k_4}\left(1 + \frac{k_3[SH] + k_4}{k_1}\,\frac{1}{[ROH]}\right) \quad (20)$$

Indeed, the relative concentration [S·]/[B·] at −80° is shown to be a linear function of 1/[ROH] in Figure 2. The slope of 0.07 is approximately equal to $k_2(SH)/k_1$, since k_3/k_4 is less than 1/300 according to the studies by Walling and Padwa.[25] Thus, we conclude that the rate of hydrogen transfer from tri-*tert*-butylcarbinol is about a factor of 10^2 faster than transfer from cyclopropane.[26]

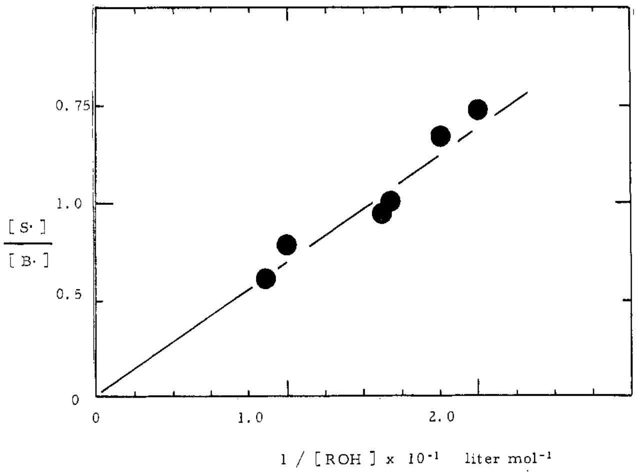


Figure 2. Relative concentrations of cyclopropyl and *tert*-butyl radicals from the reaction of tri-*tert*-butylcarbinol and *tert*-butoxy radical in cyclopropane solution at −80°. The linear plot was constrained to pass close to the origin, since $k_2[SH]/k_4$ in eq 20 is small.

Although the foregoing conclusion is based on the competitive kinetic scheme presented in eq 15–19, it is not necessary that the hydrogen transfer from the alcohol lead *directly* to an alkoxy radical as given in eq 15. Thus, an equivalent kinetic result is obtained if hydrogen transfer is accompanied by the simultaneous scission of the *tert*-butyl-C_α bond according to eq 21. Equation 21 is equivalent to the separate processes represented in eq 15 and 18.

$$[(CH_3)_3C]_3COH + Bu^tO\cdot \longrightarrow (CH_3)_3C\cdot + [(CH_3)_3C]_2CO + Bu^tOH \quad (21)$$

A necessary and sufficient condition for distinguishing between these two mechanisms is to show that an alkoxy radical is a discrete intermediate. The latter must be carried out by indirect experiments, since alkoxy radicals generally cannot be observed by esr studies in solution. Previous studies showed that trialkyl phosphites are efficient traps for alkoxy radicals and lead to phosphoranyl adducts III with large phosphorus splittings.[27] Griller and Ingold recently showed that the phosphorus splitting of a_P = 890.3 G for the *tert*-butoxy adduct can be resolved from that of the triptyloxy adduct produced simultaneously during the photolysis of triptyl-*tert*-butyl peroxide in the presence of triethyl phosphite.[20,28]

$$RO\cdot + P(OR')_3 \longrightarrow RO\dot{P}(OR')_3 \quad (22)$$
$$\text{III}$$

Table III
Esr Parameters of Alkoxy Adducts to Triethyl Phosphite

ROOR′ source						Hyperfine splitting	
R	R′	Registry no.	Solvent[a]	Phosphoranyl adduct $RO\dot{P}(OEt)_3$	Registry no.	a_P, G[b]	$\langle g\rangle$[c]
$(CH_3)_3C$	$(CH_3)_3C$	110-05-4	C–ROH	$(CH_3)_3C$	36761-40-7	884.6	2.003
$(CH_3)_3C$	$(CH_3)_3C$		C–MeOH	$(CH_3)_3C$		886.0	
$(CH_3)_3C$	$(CH_3)_3CC(CH_3)_2$	6766-51-4	C	$(CH_3)_3C$		882.7	
$(CH_3)_3C$	$(CH_3)_3CC(CH_3)_2$			$(CH_5)_3CC(CH_3)_2$	51392-68-8	897.0	2.003
CH_3	$(CH_3)_3C$	51392-67-7	C	$(CH_3)_3C$[d]		884.6	
$CH_3CH_2C(CH_3)_2$	$CH_3CH_2C(CH_3)_2$	20639-96-7	C	$CH_3CH_2C(CH_3)_2$	51392-69-9	887.4	2.003

[a] C = cyclopropane, ROH = triptyl alcohol. [b] Corrected to second order. [c] Corrected to second order using the Breit–Rabi equation: P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967. [d] Methoxy adduct may be unresolved.

We have been unable to trap triptyloxy radical as a phosphite adduct during photolysis of various mixtures of triptyl alcohol, DTBP, and triethyl phosphite at different temperatures. The esr spectrum consisted of the superposition of the spectrum of the *tert*-butoxy adduct III in Table III and that of the *tert*-butyl radical. The origin of the latter is ambiguous since it is known that the *tert*-butoxy adduct III (R = *tert*-butyl; R′ = ethyl) affords *tert*-butyl radicals by a competitive β-scission.[27] In order

$$(CH_3)_3CO\dot{P}(OEt)_3 \longrightarrow (CH_3)_3C\cdot + OP(OEt)_3 \qquad (23)$$

to obviate this difficulty, we employed di-*tert*-amyl, dicumyl, and bis(trifluoromethyl) peroxides in place of DTBP, but we were unable to observe the spectrum of either the triptyloxy adduct III or *tert*-butyl radical. We have also been unable to observe the spectrum of $\alpha,\alpha,\beta,\beta$-tetramethylpropyl radical possibly derived from the scission of the triptyloxy adduct III.[29]

The results up to this point unfortunately leave open the question of whether hydrogen transfer from alcohols is synchronous with the cleavage of an alkyl group.[30] Other competing reactions notwithstanding, the absence of alkyl cleavages in benzyl- and alkyldimethylcarbinols suggests that the driving force from such a contribution is probably not large.

Summary and Conclusions

A variety of tertiary alcohols, especially those with one or more *tert*-butyl groups, are shown to be readily cleaved by photochemically generated *tert*-butoxy radicals. The reaction proceeds by hydrogen transfer from the hydroxylic function of the alcohol to *tert*-butoxy radicals. However, probing experiments have not yet proved whether hydrogen transfer and cleavage are synchronous processes. Examination of various alkoxy radicals from peroxidic precursors indicates that *tert*-butoxy is more effective than cumyloxy, *tert*-amyloxy, and trifluoromethoxy radicals. The ineffectiveness of *tert*-amyloxy radical is due to a competing β-scission. Hydrogen fluoride which is spontaneously formed from trifluoromethanol is strongly hydrogen bonded to alcohols and inhibits hydrogen transfer to trifluoromethoxy radical. Hydrogen bonding varies in alcohols owing to steric effects[32] and it may generally play a role in determining which alcohols are particularly susceptible to hydrogen transfer.[33] Quantitative knowledge of the steric crowding about the hydroxylic function and the nature of the hydrogen bonding in alcohols would help in establishing this relationship. This system merits further study to establish these points.

Experimental Section

Materials. Di-*tert*-butyl peroxide was obtained from Shell Chemical Co., repeatedly washed with water, dried over calcium chloride, passed through an activated alumina column, and redistilled at reduced pressure prior to use. Bis(trifluoromethyl) peroxide was obtained from PCR, Inc. and used as such. Di-*tert*-amyl peroxide was prepared by the procedure of Raley, Rust, and Vaughan,[34] and was redistilled *in vacuo* and finally purified by elution of a pentane solution from an activated alumina column. Diisopropyl peroxide was prepared by the method of Pryor, *et al.*[24] Dicumyl peroxide was obtained from Hercules Chemical Co. and purified by alumina chromatography followed by recrystallization from pentane. Triethyl phosphite from Victor Chemical Co. was distilled once at atmospheric pressure under nitrogen and then redistilled from sodium metal at reduced pressure. Triptyl-*tert*-butyl peroxide was prepared by the method of Milas and Perry[35] and purified by redistillation at reduced pressure.

Triptyl alcohol was prepared from pinacolone and methylmagnesium bromide[36] and a pure sample was separated by preparative gas chromatography on a 5 ft 15% Carbowax 20M column on 30/60 mesh Chromosorb P (AW) at 150°. Triptyl alcohol, like others in the series, is extremely hygroscopic. Methyldi-*tert*-butylcarbinol, ethyldi-*tert*-butylcarbinol, methylisopropyl-*tert*-butylcarbinol, methyl-*tert*-butylphenylcarbinol, and dimethylisopropylcarbinol were prepared, characterized, and generously donated by Dr. G. F. Meier.[37] Tri-*tert*-butylcarbinol[38] and isopropyldi-*tert*-butylcarbinol were obtained as gifts from Professor V. J. Shiner, Jr., and purified by vacuum sublimation.

Sample Preparation. Samples were prepared on a vacuum line and thoroughly degassed using freeze-pump-thaw cycles. The sample composition, which consisted usually of 50–100 mg of alcohol: 0.2 ml of peroxide:1.5 ml of cyclopropane, was varied when necessary to optimize the signal-to-noise ratio. For trapping experiments the amount of triethyl phosphite added was varied from 0.05 to 0.2 ml for the above sample composition. For kinetic measurements, milligram quantities of tri-*tert*-butylcarbinol were transferred to the sample tubes by addition of a known volume of a standard solution of the alcohol in a volatile solvent (usually acetone) and removing it in vacuo. Di-*tert*-butyl peroxide (0.1 ml) was then added and after degassing cyclopropane was condensed into the tube to make the volume up to 1 ml at −78°.

Esr Measurements. The modified Varian X-band spectrometer, microwave frequency measurements, light source, and sample tubes were as described previously.[39] Perylene cation radical (g = 2.00258)[40] was used as a standard for the g-value measurements in the configuration employed. The temperature measurements in the esr tube were calibrated with a thermocouple and are accurate to 5°. The ratios of $[S\cdot]/[B\cdot]$ for the kinetic experiments were determined by averaging ten consecutive measurements of the relative intensities of selected esr lines for the different radicals, and correcting for their different degeneracies. The absence of line broadening by saturation or overmodulation was clear from the well-resolved second-order splittings in the concentration range studied. Since prolonged photolysis is expected to deplete the concentration of the alcohol, an experiment was conducted to follow the change of $[S\cdot]/[B\cdot]$ with time of photolysis. The change after ten consecutive scans was found to be insignificant, compared to other experimental scatter and variations. An average for these ten values was employed rather than a value extrapolated to zero time.

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(29) It would be desirable to pursue this point with the use of isotopically (deuterium) labeled DTBP, since structural modifications of the peroxide apparently cause other complications described above.

(30) The trapping of triptyloxy by phosphite during photolysis of triptyl-*tert*-butyl peroxide[20] is not necessarily related to the production of free triptyloxy radicals, since the reaction may proceed *via* a peroxide–phosphite exciplex, reminiscent of the transition state in the well-known thermal reaction between phosphites and peroxides.[31] Trapping of triptyloxy derived from triptyl alcohol as a free alkoxy radical is less ambiguous.

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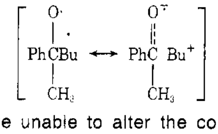

$$\left[\begin{array}{c}\mathrm{O}\cdot\\ |\ \cdot\\ \mathrm{PhCBu}\\ |\\ \mathrm{CH_3}\end{array} \longleftrightarrow \begin{array}{c}\mathrm{O}^{\cdot-}\\ \|\\ \mathrm{PhC\ \ Bu^+}\\ |\\ \mathrm{CH_3}\end{array}\right]$$

However, we were unable to alter the course of fragmentation in basic solvents such as ammonia and tetrahydrofuran to observe the spectrum of acetophenone ketyl.

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Organic Peroxides. X. Kinetics of Decomposition of Some Acyl-*p*-nitrobenzoyl Peroxides Containing Neophyl Groups

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The kinetics of the thermal decompositions of a series of mixed β-(S-phenyl)isovaleryl *p*-nitrobenzoyl peroxides (S = *p*-NO_2, *m*-Br, *p*-Cl, H, *p*-CH_3, and *p*-OCH_3) in cyclohexane and in ethylbenzene were determined iodometrically in the temperature range 60–85° and at concentrations in the 0.002–0.02 *M* range. (Evidence is presented which shows that these peroxides initially form the carboxy-inversion compounds in good yield.) At these low concentrations, the kinetics (in both solvents) were found to be accurately first order, except in decompositions of the peroxide for which S = *p*-NO_2, in which case the first-order plots were curved so as to suggest a first plus higher order induced decomposition. The mathematical method used to correct for induced decomposition is presented. For the data obtained on the decompositions of five compounds at 75° in cyclohexane, an excellent correlation is obtained between log k_d and Hammett σ's, when the corrected value of k_d for the peroxide for which S = *p*-NO_2 is used, giving $\rho = -0.76 \pm 0.02$ ($r = 0.999$). However, for the data obtained at five temperatures in ethylbenzene, log k_d correlates better with σ^+ ($r > 0.992$) than with σ (*r* values near 0.97 at all five temperatures). The ρ values for the σ^+ correlations are −0.89, −0.85, −0.81, −0.77, and −0.74, respectively, at 60, 65, 70, 75, and 80°. The activation parameters obtained for the decompositions of these peroxides show good isokinetic behavior, with β = 214°. The rate constants obtained in ethylbenzene were extrapolated to 120° for comparison with rate constants obtained at that temperature on the decompositions of the corresponding *tert*-butyl peroxy esters by Rüchardt and Hecht. Although a log–log plot of the (extrapolated) peroxide and perester rate constants is not linear, a good correlation is obtained when log $[k_{\mathrm{peroxide}}/k_{\mathrm{perester}}]$ is plotted against σ. The value of $(\rho_{\mathrm{peroxide}} - \rho_{\mathrm{perester}})$ obtained from this correlation (−0.61) indicates more sensitivity to substituents in the peroxide than in the perester series. Although this shows that the peroxide decompositions have more polar character than the decompositions of the peresters, the kinetics data presented here do not clearly delineate between identical and different transition states for the homolytic and carboxy-inversion product forming reactions of the β-phenylisovaleryl *p*-nitrobenzoyl peroxides.

The formation of carboxy-inversion compounds in decompositions of diacyl peroxides has been the subject of a number of investigations during the past two decades.[3] Although some of the details involved in the mechanism