Positive Halogen Compounds. XIII. *t*-Butyl Hypochlorite Chlorination of Ethers, Aldehydes, and Other Molecules with Polar Substituents[1]

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Abstract: Aldehydes and ethers are highly reactive toward *t*-butoxy radicals from *t*-butyl hypochlorite. Products are acid chlorides and α-chloro ethers, respectively. Significant β scission of α-alkoxy radicals from ethers (to give alkyl chloride and carbonyl compound) is observable even at 0° when a tertiary, secondary, or benzyl radical is eliminated. No comparable opening of cyclic ethers is observed under these conditions. At high concentrations, aldehydes and some ethers with *t*-butyl hypochlorite undergo a spontaneous radical-generating process in the dark, leading to induced chlorination of added hydrocarbons. Alcohols react with *t*-butyl hypochlorite by both polar and radical mechanisms. With primary alcohols the radical path predominates in nonpolar media. Similarly, ketones undergo an acid-catalyzed α-halogenation and a radical reaction giving more random substitution. Relative reactivities of a large number of molecules with polar groups are summarized and discussed.

As we have shown in previous papers,[3] radical chlorination of hydrocarbons by *t*-butyl hypochlorite is both a synthetically useful reaction and an effective technique for investigating the effect of structure on reactivity toward the chain-carrying *t*-butoxy radical. Although we have recently reported that measured relative reactivities are, in some cases, complicated by solvent effects of a still somewhat mysterious nature,[4] the perturbations are usually small and the results still of significance.

Except for a preliminary study by Walling and Jacknow,[5] some studies of epoxide chlorination,[6,7] and a reexamination of the relative reactivities of substituted toluenes,[8] radical halogenations with *t*-butyl hypochlorite have been restricted almost entirely to hydrocarbons. This paper reports results obtained with ethers, aldehydes, and some other molecules containing polar groups, intended both to determine radical products and relative reactivities and to delimit the scope of the radical process.

Results and Discussion

Ethers. Radical attack on the α hydrogens of ethers is well established as occurring in the radical addition of ethers to olefins, ether autoxidation, and photochlorination, and in various ether–peroxide reactions.[9] As anticipated, photochlorination with *t*-butyl hypochlorite also leads to facile α substitution, and results of both preparative and competitive experiments are summarized in Table I. Competitive experiments were run in benzene or chlorobenzene at hypochlorite concentrations <0.8 *M*, and followed by consumption of substrate in the usual manner.[3] Dilution was also employed in most preparative experiments since spontaneous and violent reactions occur between hypochlorite and some ethers. These spontaneous initiation processes are considered further below, but their existence suggests caution in working with hypochlorite–substrate mixtures in unexplored systems.

Table I. *t*-Butyl Hypochlorite Chlorination of Ethers at 0°

Ether	Rel. react.	Products
2,5-Dimethyltetrahydrofuran	50.5 ± 3.9	2-Chloro-2,5-dimethyltetrahydrofuran
Propylene oxide	33.6 ± 1.8	2-Chloropropylene oxide (40–50%)[a] Chloroacetone
Trimethylene oxide	33.5 ± 0.9	2-Chlorotrimethylene oxide
Dibenzyl ether	(30.3 ± 3.7)[b]	Benzaldehyde Benzyl alcohol Benzyl chloride Benzoyl chloride
Tetrahydrofuran	23.0 ± 1.1	2-Chlorotetrahydrofuran
Diethyl ether	16.3 ± 2.1	1-Chloroethyl ethyl ether
Ethylene oxide	13.1 ± 3.9	Chloroethylene oxide (90–95%)[a]
Tetrahydropyran	10.8 ± 0.5	2-Chlorotetrahydropyran
Diisopropyl ether	10.6 ± 1.4	Acetone Isopropyl chloride 2-Chloroisopropyl isopropyl ether
Cyclohexane	8.04 ± 7.0	Cyclohexyl chloride
Dioxane	6.66 ± 0.23	. . .
Methylal	6.20 ± 0.62	Methyl formate Formaldehyde Methyl chloride Chloromethyl methyl ether
Phenetole	4.37 ± 0.39	1-Chloroethyl phenyl ether
Methyl *t*-butyl ether	3.22 ± 0.07	*t*-Butyl chloride (60%) Formaldehyde *t*-Butyl chloromethyl ether
Anisole	1.01 ± 0.02	Chloromethyl phenyl ether
Toluene (std)	1.00	Benzyl chloride
Di-*t*-butyl ether	0.311 ± 0.016	. . .
t-Butyl phenyl ether	0.300 ± 0.009	. . .
Styrene oxide	0.235 ± 0.016	Phenacyl chloride
Isobutylene oxide	0.204 ± 0.003	. . .
t-Butylbenzene	0.170 ± 0.008	. . .

[a] See ref 6. [b] Questionable value, see text.

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[1] Taken from the Ph.D. Dissertation of M. J. Mintz, Columbia University, 1965. Support of the work by a grant from the National Science Foundation is gratefully acknowledged.

[2] National Science Foundation Predoctoral Fellow, 1961–1964.

[3] C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960), and subsequent papers.

[4] P. J. Wagner and C. Walling, *ibid.*, **87**, 5179 (1965).

[5] C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

[6] C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962).

[7] G. A. Razuvaev, V. S. Etlis, and N. N. Trofimov, *Zh. Organ. Khim.*, 1, 2128 (1965).

[8] R. D. Gilliom and B. F. Ward, Jr., *J. Am. Chem. Soc.*, **87**, 3944 (1965).

[9] C. Walling, "Free Radicals in Solution, " John Wiley and Sons, Inc., New York, N. Y., 1957.

Considering first the relative reactivity data of Table I, we see that reactivities per hydrogen show the expected order primary < secondary < tertiary with considerable activation of α hydrogens compared with simple hydrocarbons (*e.g.*, per hydrogen diethyl ether is about six times as reactive as cyclohexane). In contrast, β hydrogens are less reactive than those of comparable hydrocarbons (per H, cyclohexane is 40 times as reactive as di-*t*-butyl ether, compared with a secondary:primary reactivity of about 12 for hydrocarbons[3]). All these results are consistent with previous work and the generally accepted conclusion that *t*-butoxy radicals are electron-accepting species which preferentially attack points of high electron availability. In the case of dioxane, where every hydrogen is α to one oxygen and β to another, two effects compensate and reactivity per hydrogen is only slightly greater than in cyclohexane.

The α hydrogens of phenyl ethers are slightly deactivated (2–3 fold, comparing anisole and phenetole with methyl *t*-butyl ether and diethyl ether, respectively) as might be expected since phenyl is an electron-withdrawing group and decreases the electron availability of the ether oxygen. Phenyl *t*-butyl ether, however, appears anomalously reactive compared with either *t*-butylbenzene or di-*t*-butyl ether.

Reactivities of cyclic ethers vary significantly with ring size in the order 4 > 5 > 6. In fact, the spread in α-hydrogen reactivity must be even larger than indicated, since small but increasing amounts of substitution of other hydrogens must accompany increasing ring size. Results parallel electron availability as judged by ether basicity,[10] but a study of the *t*-butoxy radical reaction at 145–150° has indicated the order $5 > 6 \gg 4$.[11] However, since the latter was based on indirect measurement using *t*-butyl alcohol–acetone ratios, the discrepancy may come from solvent effects on the *t*-butoxy radical cleavage,[12] and the matter was not investigated further. Epoxides proved difficult to study accurately because of the mixture of products formed, and yielded rather puzzling results. Ethylene oxide is almost as reactive as diethyl ether, and shows no drastic drop in reactivity in a three-membered ring system as is observed with cyclopropane compared with other cycloalkanes.[6] In propylene oxide a methyl group increases reactivity, but, rather inexplicably, isobutylene oxide and styrene oxide are strongly deactivated while stilbene oxide (not included in the table) appears to be inert to *t*-butyl hypochlorite.

Major products of chlorination were identified for most of the compounds listed in Table I, and plainly arise either from the simple halogenation chain leading to α-chloro ether

$$t\text{-BuO}\cdot + \mathrm{R_1OCH_2R_2} \longrightarrow t\text{-BuOH} + \mathrm{R_1O\dot{C}HR_2} \tag{1}$$

$$\mathrm{R_1O\dot{C}HR_2} + t\text{-BuOCl} \longrightarrow \mathrm{R_1OCHClR_2} + t\text{-BuO}\cdot \tag{2}$$

or *via* β scission of the intermediate α-alkoxyalkyl radical

$$\mathrm{R_1O\dot{C}HR_2} \longrightarrow \mathrm{R_2CHO} + \mathrm{R_1}\cdot \tag{3}$$

$$\mathrm{R_1}\cdot + t\text{-BuOCl} \longrightarrow \mathrm{R_1Cl} + t\text{-BuO}\cdot \tag{4}$$

Such β scission is well known in a variety of higher temperature reactions[13] and here would give rise to alkyl halides and carbonyl compounds among the reaction products (the formation of alkyl halides provides the most unequivocal demonstration, since carbonyl compounds could arise from the facile solvolysis of α-chloro ethers during work-up). Such products do in fact appear in the chlorination of dibenzyl ether, methyl *t*-butyl ether, methylal, and, to a lesser extent, from diisopropyl ether. Yields must obviously depend on hypochlorite concentration, since the lifetime of the intermediate α-alkoxyalkyl radicals is determined by reaction 2, but at an initial concentration of hypochlorite of 0.2 *M* methyl *t*-butyl ether undergoes approximately 60% β scission. With methylal, the major cleavage products are methyl formate and methyl chloride, indicating predominant attack on the doubly activated methylene, consistent with expectations and the results of methylal addition to olefins such as ethylene.[14] Although the reactions of dibenzyl ether are complicated and are discussed further below, the results in general indicate that ease of β scission of α-alkoxy radicals parallels the stability of the radical split off (tertiary, benzyl > secondary > primary) as in the case of alkoxy radical decompositions[15] and that, with suitable structures, the reaction is surprisingly important even at 0°.

In interesting contrast, no β scission could be detected with the cyclic ethers (except possibly epoxides) under our conditions. We have subsequently observed a similar difference in the reactions of cyclic and noncyclic ethers with peroxides at 75–100°,[16] although opening of cyclic ethers by *t*-butoxy radicals has been reported at 145–150°.[17] A possible explanation is that the β scission is reversible, and reclosure is observable when the resulting fragments are part of the same molecule and cannot diffuse apart. Such a proposal is consistent with Menapace and Kuivila's observation of the formation of 2-phenyltetrahydrofuran in the tributylin hydride reduction of γ-chlorobutyrophenone.[18] On the other hand, no reclosure to an ether structure has been noted following the β scission of cycloalkyloxy radicals such as the 1-methylcyclopentoxy radical,[15] so that the range of conditions under which reclosure may occur remains ill defined.

Although the primary product of ethylene oxide chlorination is chloroethylene oxide, the compound rearranges slowly to α-chloroacetaldehyde on standing in $\mathrm{CCl_4}$ at room temperature, a process analogous to the epoxide–ketone rearrangement proposed by McDonald and Schwab to take place during the attempted preparation of chlorinated stilbene oxides.[19] Chloroacetone is a minor product in the *t*-butyl hypochlorite chlorination of propylene oxide, while we find phenacyl chloride as the sole product from styrene oxide. Although these products indicate the point of *t*-butoxy radical attack as occurring at the more substituted carbon, as also reported by Razuvaev,[7] it is not evident

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[10] H. S. Gutowsky, R. L. Rutledge, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **76**, 4242 (1954).

[11] T. J. Wallace, Thesis, University of Connecticut, 1960.

[12] C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

[13] P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

[14] C. Aldridge, J. Zachry, and E. Hunter, *J. Org. Chem.*, **27**, 47 (1962).

[15] C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963).

[16] J. Azar, Thesis, Columbia University, 1966.

[17] T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **27**, 3067 (1962). Opening of cyclic acetals is also known; *cf.* E. S. Huyser and Z. Garcia, *ibid.*, **27**, 2716 (1962). Here, however, opening yields an ester rather than a simple carbonyl group.

[18] L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

[19] R. N. McDonald and P. A. Schwab, *ibid.*, **85**, 4004 (1963).

Table II. Products of Alcohol Oxidation by *t*-Butyl Hypochlorite

Alcohol	Products
Methyl	Formaldehyde Methyl formate
Ethyl	Acetaldehyde Ethyl acetate
Benzyl	Benzaldehyde Benzoyl chloride *t*-Butyl benzoate
Isopropyl	Acetone (60%) Chloroacetone (20%)
sec-Butyl	Butanone (60%) Chlorobutanones (20%)
Benzhydryl	Benzophenone

Table III. Oxidation of *sec*-Butyl Alcohol by *t*-Butyl Hypochlorite[a]

Solvent	Time, min
Acetonitrile	1.5
Benzene	2.5
CCl_4	11
Cyclohexane	25

[a] 1.3 *M* alcohol, 0.42 *M* hypochlorite at room temperature. Time is that required for complete loss of oxidizing power of solution.

from our data whether they arise from ring opening of the intermediate radical, or *via* subsequent rearrangement. Finally, chlorination of dibenzyl ether yielded anomalous results indicating the formation of molecular chlorine, since in the presence of the ether mesitylene undergoes nuclear chlorination and 2,3-dimethylbutane shows a substitution pattern characteristic of a chlorine atom chain. This complication, not observed with other ethers, may arise from the facile alcoholysis of the highly reactive α-chlorobenzyl ether by *t*-butyl alcohol and reaction of the HCl liberated with hypochlorite to yield molecular chlorine. Once formed, the chlorine produces more HCl in its reactions and is continuously regenerated. Because of this difficulty, the relative reactivity result for dibenzyl ether is questionable.

Aldehydes and Alcohols. The facile reaction of *t*-butyl hypochlorite with aromatic aldehydes to yield acid chlorides has been noted by Ginsberg.[20] We find that aliphatic aldehydes behave similarly, acetaldehyde giving acetyl chloride as the sole product, and even acrolein yielding acrylyl chloride in 55% yield.[21] The reactions are apparently spontaneously initiated radical chains, at least at high concentrations, and were run in dilute solution (<0.25 *M*) in benzene or chlorobenzene. Competitive reactions indicated relative reactivities acetaldehyde:benzaldehyde:cyclohexane 4.27 ± 0.32:3.43 ± 0.28:1.00.[22] The selectivity of the reaction suggests its synthetic value, and the higher reactivity of the aliphatic aldehyde parallels behavior in autoxidation.[23] The oxidation of alcohols by *t*-butyl hypochlorite is a well-known process, and early work has been reviewed by Anbar and Ginsberg,[24] although there has been no detailed study of mechanism. Products of our own studies are listed in Table II and correspond to those in the literature. The complicated mixtures from primary alcohols undoubtedly arise from further reaction of intermediate aldehydes.

The rates of reaction of secondary alcohols appear independent of light or oxygen, and are faster in polar than in nonpolar solvents (Table III). Results suggest some sort of direct initial polar reaction similar to that proposed for the bromine oxidation of secondary alcohols,[25] together with further oxidation by molecular chlorine liberated by the HCl produced.[26] The alternate of an initial exchange to yield a secondary hypochlorite which subsequently decomposes as suggested by Anbar and Ginsberg[24] seems unlikely, for while 0.4 *M* *t*-butyl hypochlorite oxidizes 0.4 *M* isopropyl alcohol in benzene at room temperature in less than 3 min, 0.4 *M* isopropyl hypochlorite requires over 30 min for decomposition. The failure of *t*-butyl hypochlorite to exchange with a *tertiary* alcohol was demonstrated in an even more conclusive manner, based upon the observation[15] that, while *t*-butyl hypochlorite chlorinates a mixture of cyclohexene and cyclohexane to cyclohexenyl and cyclohexyl chlorides, benzyldimethylcarbinyl hypochlorite, in the same medium, undergoes clean β scission to benzyl chloride and acetone. Mixtures of *t*-butyl hypochlorite with benzyldimethylcarbinol and of *t*-butyl alcohol with benzyldimethylcarbinyl hypochlorite in cyclohexane containing cyclohexene were allowed to stand for several hours at room temperature and then decomposed photochemically at 0°. The former yielded C_6 chlorides, the alcohols, and no benzyl chloride, the latter benzyl chloride and no C_6 chlorides. Similar experiments in the presence of pyridine or trifluoroacetic acid to catalyze exchange gave similar results.

In contrast, hypochlorite reactions with primary alcohols are sensitive to both oxygen and light. For example, degassed tubes containing ethanol and hypochlorite in benzene reacted completely in 15 min at 0° on irradiation, but showed negligible decomposition in the same period in the dark. Also, photochlorination of methanol was significantly retarded by oxygen. Competitive reactions with cyclohexane further indicated a radical process since cyclohexyl chloride was produced, and yielded the plausible reactivity series ethyl alcohol:*n*-propyl alcohol:benzyl alcohol:cyclohexane, 0.94 ± 0.07:0.84 ± 0.09:1.82 ± 0.24:1.0. Although competitions were run in dilute solution to minimize any effect of HCl produced, some contribution from a chlorine atom chain may be involved. On the other hand, reaction of benzyldimethylcarbinyl hypochlorite with ethanol in the presence of cyclohexene gave over 90% benzyl chloride showing neither appreciable halogen exchange or chlorine atom participation in this case.

Other Substrates. Relative reactivities and products from reaction of *t*-butyl hypochlorite with a number of other substrates, chiefly with electron-withdrawing groups, are listed in Table IV. Most of the result are straightforward and simply point up the deactivating effect of electronegative groups. Thus attack on

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(20) D. Ginsberg, *J. Am. Chem. Soc.*, 73, 702 (1951).

(21) This reaction has been reported previously: C. E. Castro and J. K. Kochi, U. S. Patent 3,075,000 (Jan 22, 1963).

(22) Obtained from competitions acetaldehyde–benzaldehyde and acetaldehyde–tetrahydrofuran. Experiments using cyclohexene as a standard gave even higher reactivities, but inconsistent results.

(23) C. Walling and E. A. McElhill, *J. Am. Chem. Soc.*, 73, 2927 (1951).

(24) M. Anbar and D. Ginsberg, *Chem. Rev.*, **54**, 925 (1954).

(25) I. R. L. Barker, W. G. Overend, and C. W. Rees, *J. Chem. Soc.*, 3263 (1964).

(26) The role of chlorine is supported by the observation that the oxidations show an induction period eliminated by the addition of a trace of HCl.

Table IV. Relative Reactivities and Products from *t*-Butyl Hypochlorite Chlorination of Various Substrates at 0°

Compound	Rel. react.	Products
Cyclohexene	48.7 ± 1	. . .
Cyclohexane	8.07 ± 0.7	. . .
2,3-Dimethylbutane	5.35 ± 0.6	1-Chloro-2,3-dimethylbutane (8%) 2-Chloro-2,3-dimethylbutane (92%)
Methyl formate	2.14 ± 0.2	Methyl chloroformate
Cyclopentanone	1.53[a]	2-Chlorocyclopentanone (48%) 3-Chlorocyclopentanone (52%)
Chloroform	1.08 ± 0.05	Carbon tetrachloride
Toluene (std)	1.00	
3-Pentanone	0.92 ± 0.02	2-Chloro-3-pentanone (86%) 1-Chloro-3-pentanone (14%)
Methylene chloride	0.234 ± 0.016	Chloroform
Acetone	0.17 ± 0.02	Chloroacetone
Ethyl acetate	0.156 ± 0.002	*b*
t-Butyl alcohol	0.129 ± 0.003	1-Chloro-2-methyl-2-propanol
Acetophenone	0.107 ± 0.016	Phenacyl chloride
Ethyl benzoate	0.093 ± 0.009	*b*
Methyl benzoate	0.040 ± 0.005	*b*
Phenyl acetate	0.029 ± 0.003	Phenyl chloroacetate

[a] At 40°.[5] [b] Products not investigated, but *n*-propyl accetate undergoes predominantly substitution on the α and β positions of the propyl group.[5]

methyl formate occurs at the formyl hydrogen, but $^1/_{16}$ as readily as attack on acetaldehyde. Again, hydrogens of methylene chloride are 0.174 as reactive as those of cyclohexane and that of chloroform 0.44 as reactive as the tertiary hydrogens of 2,3-dimethylbutane.

Additional quantitative relations are considered in the next section, but, comparing 3-pentanone and cyclopentanone with 2,3-dimethylbutane and cyclohexane, it is evident that deactivation by the carbonyl group extends to β as well as α hydrogens.

Halogenation of ketones deserves a final comment. Our results in nonpolar solvents are those of the radical chain process. In polar solvents, or in the presence of acid catalysts, *t*-butyl hypochlorite chlorinates ketones by a polar mechanism to yield α-chloro ketones.[24] We have confirmed this in several cases, *e.g.*, in acetic acid cyclopentanone reacts rapidly in the dark to give solely 2-chlorocyclopentanone.

Summary of Relative Reactivity Data. Since the work reported here represents the conclusion, at least for the time being, of our general survey of relative reactivities in the reactions of *t*-butoxy radicals, we present a summary in Table V of the effects of the more important types of substituents on the reactivities of C–H bonds toward *t*-butoxy radical attack. The purpose is both to characterize *t*-butoxy radical selectivity for comparison with series in the literature for other radicals, and to provide a useful guide for the synthetic use of *t*-butyl hypochlorite chlorination. Data are in general at 0° in inert solvents. Selectivities are known to decrease moderately with increasing temperature and to vary slightly with solvent.[3,12] There are also known, but not clearly understood, differences between results obtained by direct competitions and those calculated indirectly by comparing yields of *t*-butyl alcohol and acetone.[4] Data given here are from direct competitions, since these determine actual products in synthetic use.

Table V. Summary of Structural Effects on Reactivity of C–H Bonds toward *t*-Butoxy Radicals[a]

R	$\underset{\text{H}}{\underset{\vert}{\text{RCH}_2}}$	$\underset{\text{H}}{\underset{\vert}{\text{RCHCH}_3}}$	$\underset{\text{H}}{\underset{\vert}{\text{RC(CH}_3\text{)}_2}}$	$\underset{\text{H}}{\underset{\vert}{\text{RC=O}}}$
Alkyl	1.00	12.8	68	103
Phenyl	6.4	45[b]	77	82
Vinyl[c]	12	61	176	. . .
Cl-	. . .	5.1[d]	. . .	. . .
RO-	21	78	91	6.4
RCO-	0.55	3.8	. . .	. . .
ROCO- HOCO- NC-	0.19[e]	0.67[f]	. . .	

[a] At 0° in inert solvent by direct competition unless indicated. [b] Calculated from indirect reactivity data in chlorobenzene.[4] [c] At 40°, substitution on vinyl group increases reactivity further: C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961). [d] Calculated from 1-chlorobutane at 40°.[5] [e] Phenyl acetate. Indirect measurements indicate <<0.1 for acetic acid and acetonitrile.[4] [f] Butyronitrile data at 40°.[5]

Inspection of the table emphasizes the high selectivity of *t*-butoxy radicals, both in the usual series tertiary > secondary > primary and in their sensitivity toward electron-supplying and electron-withdrawing substituents. As we have noted before, electron availability appears to play a more important role than C–H bond strength and probably contributes the major part of the tertiary > secondary > primary selectivity noted. Qualitatively, results remain consistent with the idea that polar contributions to the transition state

$$\text{BuO}\cdot\ \text{H–R} \longleftrightarrow \text{BuO}^-\ \dot{\text{H}}\ {}^+\text{R} \longleftrightarrow \text{BuO–H}\ \cdot\text{R} \qquad (5)$$

play an important role in determining reaction rates, although investigations of the Hammett ρ–σ relation in the reactions of substituted toluenes have so far given conflicting results.[5,8] Without such contributions it is difficult to understand the very high reactivities of ethers and aldehydes, and it is interesting that, with molecules containing the RCHO group, phenyl and RO act simply as deactivating groups.

Spontaneous Initiation Processes. As noted above, spontaneous reactions occur on mixing *t*-butyl hypochlorite with aldehydes and some ethers, even in the dark and absence of known initiators. In undiluted systems, using benzaldehyde, tetrahydrofuran, or diethyl ether the reaction at room temperature is violently exothermic but inhibited by oxygen or 2,4,6-tri-*t*-butylphenol. Products are benzoyl chloride and the α-chloro ethers, plus *t*-butyl alcohol and acetone, but, since some HCl is liberated, participation of molecular chlorine cannot be excluded.

At 0° small samples in a cooling bath react slowly and controllably and no HCl is formed. The system also induces the chlorination of other hydrocarbons, and it was shown that the usual *t*-butoxy radical chain is involved under these conditions by examining the product distribution obtained on adding a mixture of cyclohexane and 2,3-dimethylbutane. Both tertiary: primary ratios for the butane and relative reactivities of the two hydrocarbons agreed with those obtained in the ordinary photoreaction in the absence of aldehyde or ether.

Spontaneous radical formation from *t*-butyl hypochlorite in the presence of certain acetylenes has been reported previously,[27] together with evidence for a chlorine atom transfer mechanism possibly concerted

$$t\text{-BuOCl} + \text{RC}{\equiv}\text{CR} \longrightarrow t\text{-BuO}\cdot + \text{RCCl}{=}\dot{\text{C}}\text{R} \qquad (6)$$

with addition of the *t*-butoxy radical to another molecule of acetylene. A comparable termolecular process involving C–H bond cleavage is energetically feasible here, *e.g.*

$$2t\text{-BuOCl} + \text{RCHO} \longrightarrow 2t\text{-BuO}\cdot + \text{HCl} + \text{RCOCl} \qquad (7)$$

and "charge transfer" structures can easily be drawn as contributing to stabilization of the transition state. However, this provides strictly an *ad hoc* explanation, and the problem of such spontaneous initiation processes invites further study.[28]

Experimental Section

Reagents. Solvents and reactants either were commercial materials or were prepared by well-established methods. Physical constants were checked and, in general, purity confirmed by gas-liquid partition chromatography (glpc).

Competitive experiments were carried out as in previous papers in this series,[3] using small sample in sealed, degassed tubes and irradiating in a 0° thermostat with an incandescent lamp. Benzene, chlorobenzene, or *o*-dichlorobenzene were used as diluents to avoid rapid spontaneous reaction. Relative reactivities were calculated from disappearance of substrate (or, in some cases, appearance of products) by glpc analysis *vs.* internal standards with calibration as required. Comparisons were always between substrates of similar reactivity (preferably within a factor of 4), and referred back to standard (toluene or cyclohexane) in a stepwise manner. Since the whole sequence involved some 86 comparisons (all in duplicate to quadruplicate) individual experiments are not listed, but only experimental uncertainties (mean deviations) using standard formulas for the propagation of errors. Calculation of relative reactivities for *t*-butyl alcohol and acetone were corrected for the fact that they are produced as well as being consumed during the reaction.

Products were determined from reactions run either in sealed tubes or small flasks. Since α-chloro ethers are highly unstable, they were usually identified by hydrolysis to the carbonyl compound and comparison of derivatives with authentic materials. Acid chlorides were similarly converted to methyl esters. Other products were separated by glpc, collected, and identified by infrared spectra or other physical properties. In ether halogenations leading to β scission, the amount of alkyl chloride produced was used as the measure of the β-scission process.

Halogenation of Ketones. *t*-Butyl hypochlorite reacts rapidly with acetone in the dark in the presence of trifluoroacetic acid (1:10:0.1) to give chloroacetone and *t*-butyl alcohol in almost quantitative yield in less than 3 hr. Similarly, cyclopentanone (2 ml), hypochlorite (0.5 ml), and acetic acid (5 ml) give 2-chlorocyclopentanone quantitatively in less than 1.5 hr. Degassed solutions of hypochlorite in cyclopentanone are stable in the dark at 0° but react on irradiation. Glpc analysis yielded 2-chlorocyclopentanone and cyclopenten-3-one. The unsaturated ketone was assumed to come from 3-chlorocyclopentanone, since it was not present in the reaction mixture and since the 2-chloro ketone is stable under the analysis conditions. With 3-pentanone, both chloro products were stable and could be isolated.

The ratio of products from cyclopentanone remained constant when treated as described, in the presence of $NaHCO_3$, pyridine, or in refluxing Freon 11 to sweep out any HCl formed. Accordingly we conclude that they arise solely from the radical process.

Spontaneous Initiation Experiments. *t*-Butyl hypochlorite (0.7 ml) was added to a mixture of 1 ml each of freshly distilled benzaldehyde, cyclohexane, and 2,3-dimethylbutane at 0° under a N_2 atmosphere. After 1 hr the residual hypochlorite was destroyed with H_2O–KI and the organic layer analyzed by glpc for cyclohexyl chloride and the two chloro-2,3-dimethylhexanes. Because of the high reactivity of benzaldehyde, only very small quantities of the chlorides were present (about 4% total yield). Relative yields were cyclohexyl chloride 68%, 2-chloro-2,3-dimethylbutane 29%, and 1-chloro-2,3-dimethylbutane 3%. A similar experiment using diethyl ether in place of benzaldehyde gave 61.37 and 2%, respectively, but an even lower total yield. Both results agree, within experimental uncertainty because of the low yields, with photoinitiated reactions in the absence of aldehyde or ether (61, 36, and 3%, respectively).

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[27] C. Walling, L. Heaton, and D. D. Tanner, *J. Am. Chem. Soc.*, **87**, 1715 (1965).

[28] In particular, spontaneous processes involving molecular chlorine occur with olefins (where hypochlorite is stable) but not with acetylenes or ethers; *cf.* M. Poutsma, *ibid.*, **87**, 2161, 2172 (1965).

Communications to the Editor

Stereochemistry of Asymmetric Silicon. Stereospecific Platinum-Catalyzed Hydrosilation of 1-Octene with Optically Active R_3Si^*H[1,2]

Sir:

The first example of hydrosilation, addition of a silicon hydride to an olefin, involved reaction of trichlorosilane with 1-octene in the presence of diacetyl peroxide and was reported in 1947.[3] During the next two decades hydrosilation became an exceedingly important laboratory and industrial process, and it was discovered that platinum–charcoal and chloroplatinic acid are very effective catalysts.[4]

$$\equiv\text{SiH} + \text{CH}_2{=}\text{CH}{-}\text{R} \xrightarrow[\text{H}_2\text{PtCl}_6]{\text{Pt–C} \atop \text{or}} \equiv\text{SiCH}_2\text{CH}_2\text{R} \qquad (1)$$

Beginning with the observation that primary alkylsilanes often result from reactions involving nonterminal olefins, as in reaction 2,[5] Speier and co-workers

$$\text{Cl}_2(\text{CH}_3)\text{SiH} + \text{CH}_3\text{CH}{=}\text{CHCH}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{PtCl}_6} \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2 \qquad (2)$$

have engaged in an intensive study of the mechanism of reactions 1.[6] This work revealed that platinum-catalyzed hydrosilation is often accompanied by olefin isomerization which is significantly altered by the presence of silane,[6a–c] and that hydrosilation carried out with Cl_3SiD results in extensive exchange between Si–D and C–H of the olefin plus the formation of adducts having deuterium widely distributed in their structures, as in reaction 3.[6c]

$$3.56\text{Cl}_3\text{SiD} + \text{CH}_2{=}\text{C}(\text{CH}_3)_2 \xrightarrow{\text{H}_2\text{PtCl}_6} \text{Cl}_3\text{SiC}_4\text{H}_{6.5}\text{D}_{2.5} + 1.5\text{Cl}_3\text{SiH} + \text{Cl}_3\text{SiD} \qquad (3)$$

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[2] Work carried out in part at The Pennsylvania State University.

[3] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947).

[4] For an excellent review up to about 1959, see C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp 45–64.

[5] J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

[6] (a) J. L. Speier and J. C. Saam, *ibid.*, **80**, 4104 (1958); (b) *ibid.*, **83**, 1351 (1961); (c) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964); (d) M. C. Musolf and J. L. Speier, *J. Org. Chem.*, **29**, 2519 (1964); (e) J. W. Ryan and J. L. Speier, *ibid.*, 31, 2698 (1966).