Studies of the Chlorination of the Carboxylic Acids with *t*-Butyl Hypochlorite

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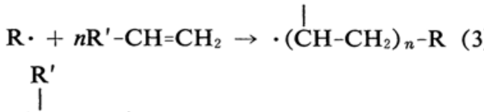
Investigations of chlorination with *t*-butyl hypochlorite have been carried out for many years; recently Walling and his co-workers have indicated that the above hypochlorite is an efficient free-radical chlorinating agent for various hydrocarbons.[1-3]

We have been making studies of the extensive utilization of *t*-butyl hypochlorite, which can readily seprepared from *t*-butyl alcohol, in synthetic organic chemistry. As a part of these studies, our attention has been drawn to the telomerization using *t*-butyl hypochlorite.

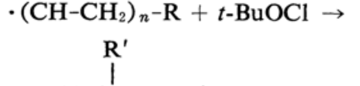
In general, it is well-known that, with the exception of a few cases of using some such reagents as carbon tetrachloride or cyanogen chloride as a telogen, the telomerization affords a telomer with only one functional group, as is shown in the reactions of olefins with *N*-alkyl substituted formamides, acetic acid or alkyl acetates in the presence of di-*t*-butyl peroxide as the initiator.[4,5] However, when this hypochlorite is used in the telomerization, one would expect that the telomer with two functional groups at the both end sites, would be obtained, as is shown in the following scheme:

$$t\text{-BuOCl} \xrightarrow{h\nu} t\text{-BuO}\cdot + \text{Cl}\cdot \qquad (1)$$

$$t\text{-BuO}\cdot + \text{RH} \rightarrow t\text{-BuOH} + \text{R}\cdot \qquad (2)$$



$$\text{R}\cdot + n\text{R}'\text{-CH=CH}_2 \rightarrow \cdot(\overset{\overset{\text{R}'}{|}}{\text{C}}\text{H-CH}_2)_n\text{-R} \qquad (3)$$



$$\cdot(\overset{\overset{\text{R}'}{|}}{\text{C}}\text{H-CH}_2)_n\text{-R} + t\text{-BuOCl} \rightarrow \text{Cl-}(\overset{\overset{\text{R}'}{|}}{\text{C}}\text{H-CH}_2)_n\text{-R} + t\text{-BuO}\cdot \qquad (4)$$

We have already demonstrated that we have succeeded in the synthesis of 5-chloro-2-pentanone by means of this new telomerization using acetone and ethylene.[6] Since the carboxylic acids as well as acetone seem to be available for the telogen, we have first investigated the reactions of *t*-butyl hypochlorite with the carboxylic acids as an experiment preliminary to the telomerization using the carboxylic acids as the telogen. Now, in this paper, we wish to describe the reactions of *t*-butyl hypochlorite with a number of carboxylic acids in the presence of a solvent such as benzene or carbon tetrachloride and, especially, to demonstrate the effects of the acidity of the carboxylic acids and those of the solvents on the reactions, as well as to demonstrate the reactivities of the *t*-butoxy radical.

Experimental

Materials. — *t*-Butyl hypochlorite was prepared according to the procedure of Teeter and Bell.[7] The hypochlorite was distilled before use; its b. p. was 79.5—80°C, and it was stored in the dark at 0°C. The purity was 95—99% as determined by iodometric analysis. The other materials were commercial-grade chemicals and were purified by the usual method and distilled or recrystallized before use.

Reaction Procedures. — All the reactions were carried out in a 200-ml. (or 300-ml.) four-necked flask equipped with a thermometer, a mechanical stirrer, a gas inlet and a condenser, to which a trap at −78°C and a gas holder were attached. *t*-Butyl hypochlorite and the carboxylic acid (and the solvent) were placed in the flask wrapped in aluminum foil designed to intercept the light. After completely replacing the system by nitrogen for 15 min. prior to irradiation, the aluminum foil was removed and the system was irradiated by a 60-watt incandescent light bulb at a distance of 5 cm. The conditions of the reaction are shown in Table I.

Analytical Procedures. — The gaseous products and the trapped fraction were analyzed by gas chromatography using a 2.5 m. silica gel and a 2.5 m. β, β'-oxydipropionitrile column. The low-boiling products and the solvent were distilled and determined quantitatively by gas chromatography using a 2.5 m. dinonyl phthalate column. Unreacted liquid carboxylic acids (acetic, propionic and *n*-butyric acids) were also distilled and titrated with 0.1 N sodium hydroxide, using phenolphthalein as

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

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

[3] C. Walling and W. Thaler, ibid., **83**, 3877 (1961).

[4] L. Friedman and H. Shechter, *Tetrahedron Letters*. 238 (1961).

[5] J. Allen, *Chem. & Ind.*, **1962**, 1621.

[6] Reported at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1964.

[7] H. M. Teeter and E. W. Bell, "Organic Synthesis," **32**, 20 (1956).

Table I. Reaction conditions[*1]

Exp. No.	Carboxylic acid	Solvent	*t*-BuOCl g. (mol.)	Carboxylic acid g. (mol.)	Solvent g. (mol.)
1	CH_3COOH	None	16.3 (0.15)	90 (1.5)	—
2	CH_3COOH[*2]	None	27.1 (0.25)	240 (4.0)	—
3	CH_3COOH	C_6H_6	21.7 (0.2)	12 (0.2)	156 (2.0)
4	CH_3COOH	CCl_4	10.9 (0.1)	6 (0.1)	154 (1.0)
5	C_2H_5COOH	None	16.3 (0.15)	111 (1.5)	—
6	C_2H_5COOH	C_6H_6	21.7 (0.2)	14.8 (0.2)	156 (2.0)
7	*n*-C_3H_7COOH	None	16.3 (0.15)	132 (1.5)	—
8	$CH_2ClCOOH$	C_6H_6	21.7 (0.2)	18.9 (0.2)	156 (2.0)
9	CCl_3COOH	C_6H_6	10.9 (0.1)	16.3 (0.1)	78 (1.0)
10	CCl_3COOH	CCl_4	16.3 (0.15)	24.6 (0.15)	115.5 (0.75)
11	None	C_6H_6	21.7 (0.2)	—	156 (2.0)

[*1] All the reactions were carried out at 30°C.

[*2] The high pressure mercury arc (Eikosha Type 400 W) was used.

an indicator. The high-boiling products were fractionally distilled under reduced pressure and determined quantitatively by gas chromatography, using a 2.5 m. dinonyl phthalate, a 2 m. polyethylene glycol-6000 or a 2.5 m. silicon DC-550 column; they were also determined qualitatively by means of their infrared spectra, by various spot tests, or by introduction to their derivatives. In the case of monochloroacetic acid, the high-boiling fractions, containing the unreacted acid, were treated with diazomethane and analyzed by gas chromatography, using a 3 m. tricresyl phosphate column. In the case of trichloroacetic acid in the presence of benzene, the low-boiling products and benzene were treated as has been described above. The residue was dissolved in water and extracted with benzene. The benzene extract was washed with 10% aqueous sodium carbonate and water successively. The residue obtained by the removal of benzene was a polymeric product; further investigation was not undertaken.

Results

Reactions with Acetic Acid. — When *t*-butyl hypochlorite was illuminated by an incandescent light bulb in the presence of acetic acid, the acid was scarcely chlorinated, whereas the self-decomposition of *t*-butyl hypochlorite proceeded predominantly. As a consequence, acetone and methyl chloride were obtained as the main products, accompanied by small amounts of *t*-butyl alcohol, monochloroacetic acid, chloroacetone and chloro-*t*-butyl alcohol. The results on acetic acid are listed in Table II.

As Table II shows, the reactions in the presence of benzene or carbon tetrachloride gave the same results as the above, except that the formation of *t*-butyl alcohol increased somewhat. Interestingly, the formation of carbon dioxide suggests that the *t*-butoxy radical generated by the decomposition of *t*-butyl hypochlorite may abstract the hydrogen of the carboxyl group.

Table II. Major products of reactions with acetic acid

Exp. No.	1	2	3	4
Product, mol. %*				
t-Butyl alcohol	16.2	16.7	35.1	32.5
Acetone	78.1	72.1	60.4	50.4
Monochloroacetone	2.9	4.8	1.6	1.1
Chloro-*t*-butyl alcohol	0.6	9.2	3.2	8.3
Monochloroacetic acid	6.4	1.3	Trace	4.2
Chlorobenzene	—	—	3.5	—
Gaseous products	CO_2 CH_3Cl	CO_2 CH_3Cl	CO_2 CH_3Cl	CO_2 CH_3Cl

* Basis on *t*-butyl hypochlorite used.

Reactions with Propionic and *n*-Butyric Acids. —Table III shows results of the reactions of *t*-butyl hypochlorite with propionic and *n*-butyric acids.

In the case of propionic acid, the major liquid products were *t*-butyl alcohol, acetone and *α*- and *β*-chloropropionic acids. The

Table III. Major products of reactions with propionic and *n*-butyric acids

Exp. No.	5	6	7
Product, mol. %*			
t-Butyl alcohol	59.4	45.3	52.3
Acetone	27.6	56.8	29.9
Monochloroacetone	5.8	Trace	2.2
Chloro-*t*-butyl alcohol	8.0	0.5	1.8
Chlorinated carboxylic acid	41.2	5.5	52.7
Chlorobenzene	—	4.9	—
Gaseous products	CO_2 CH_3Cl C_2H_5Cl	CO_2 CH_3Cl C_2H_5Cl	CO_2 CH_3Cl *n*-C_3H_7Cl

* Basis on *t*-butyl hypochlorite used.

yields of chlorinated carboxylic acids were considerably higher than those in the chlorination of acetic acid. On the other hand, in the presence of benzene as the solvent, the amounts of chlorinated carboxylic acids and *t*-butyl alcohol decreased, in contrast to an increase in those of acetone. From the formation of ethyl chloride along with carbon dioxide, we would conclude that the decarboxylation of the carboxylic acid might well occur. In Table III it can also be observed that *n*-butyric acid is more efficiently chlorinated than propionic acid by *t*-butyl hypochlorite. The isomer distributions of chlorinated carboxylic acids of propionic and *n*-butyric acids are summarized in Table IV.

TABLE IV. ISOMER DISTRIBUTIONS OF CHLORINATED CARBOXYLIC ACIDS

Exp. No.	Carboxylic acid	α-Isomer %	β-Isomer %	γ-Isomer %
5	C_2H_5COOH	61.2	38.8	—
6	C_2H_5COOH	63.2	36.8	—
7	n-C_3H_7COOH	20.6	46.4	33.0

The α-isomer was rich in the case of propionic acid, but the ratio of α- and β-isomers was constant, regardless of the presence or absence of the solvent. On the other hand, in the case of *n*-butyric acid, the β-isomer was predominantly formed and the γ-isomer was preferentially formed over the α-isomer.

Reactions with Other Acids. — All the reactions with other acids were carried out in the presence of the solvent. The major products are listed in Table V.

TABLE V. MAJOR PRODUCTS OF REACTIONS WITH OTHER ACIDS

Exp. No.	8	9	10	11
Product, mol. %*				
t-Butyl alcohol	32.4	41.9	12.6	41.8
Acetone	49.1	Trace	27.1	49.1
Monochloroacetone	1.6	Trace	28.1	1.1
Chloro-*t*-butyl alcohol	4.6	None	12.3	1.4
Chlorinated carboxylic acid	0.4	—	—	—
Chlorobenzene	6.4	41.8	—	2.2
Gaseous products	CO_2 CH_3Cl	Isobutene	CH_3Cl	CH_3Cl

* Basis on *t*-butyl hypochlorite used.

The reaction of *t*-butyl hypochlorite with monochloroacetic acid gave the same results as in the case of acetic acid in the presence of benzene with the exception of the increase in the formation of chlorobenzene. The reactions of *t*-butyl hypochlorite with trichloroacetic acid provided very interesting results. When benzene was used as the solvent, the decomposition of *t*-butyl hypochlorite began immediately, without any illumination, as soon as the hypochlorite was dropped into the flask containing benzene and trichloroacetic acid. The products were *t*-butyl alcohol, chlorobenzene and isobutene, accompanied by trace amounts of acetone. Isobutene may be formed from *t*-butyl alcohol during distillation by the acid-catalytic action of trichloroacetic acid. On the other hand, using carbon tetrachloride as the solvent, the major products were acetone, methyl chloride, *t*-butyl alcohol, chloroacetone and chloro-*t*-butyl alcohol.

Discussion

The Effects of the Acidity of Carboxylic Acids.—*t*-Butyl hypochlorite is often used as an electrophilic-chlorinating reagent in the presence of an acid-catalyst. For example, benzene has been efficiently chlorinated by *t*-butyl hypochlorite in the presence of sulfuric acid.[8] In our study, benzene was also chlorinated easily by *t*-butyl hypochlorite in the presence of trichloroacetic acid, which is a strong acid as well as a sulfuric acid, whereas scarcely any acetone was formed. From these results, it may be concluded that, in this reaction, the chlorination of benzene proceeds predominantly by the electrophilic attack of the chloro cation on the aromatic nucleus. The acidity of carboxylic acids in benzene and the yield of chlorobenzene are summarized in Table VI.

TABLE VI. THE YIELD OF CHLOROBENZENE IN THE PRESENCE OF THE CARBOXYLIC ACID

Exp. No.	Carboxylic acid	pK in C_6H_6[*1]	Yield of chlorobenzene[*2] %
3	CH_3COOH	5.18	3.5
6	C_2H_5COOH		4.9
8	$CH_2ClCOOH$	1.75	6.2
10	CCl_3COOH	0.70	41.8
11	None	—	2.2

[*1] V. K. LaMer and H. C. Dowens, *J. Am. Chem. Soc.*, **55**, 1860 (1933).

[*2] Mol. % of *t*-butyl hypochlorite used.

In Table VI it can be observed that, although chlorobenzene was formed in a 2.2% yield by the homolytic decomposition of *t*-butyl hypochlorite in benzene, the yield of chlorobenzene was higher than 2.2% in the presence of the carboxylic acid, and that the yield of chlorobenzene increased with the increase in the

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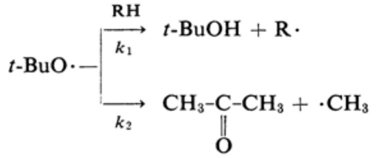
8) M. Anbar, Ph. D. Thesis, Hebrew University, Jerusalem (1953).

acidity of the carboxylic acids. Consequently, it may be presumed that the ionic process in the reaction becomes more important with the increase in the acidity of the carboxylic acids. However, in such weak acids as acetic and propionic acids, this ionic process may be almost ignored; we therefore studied in more detail the radical reactions of *t*-butyl hypochlorite with such weak acids.

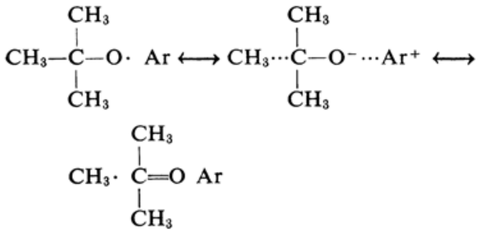
The Solvent Effects.—As is well known, the *t*-butoxy radical formed by the photo-induced chain decomposition of *t*-butyl hypochlorite abstracts hydrogen or proceeds competitively via fragmentation, as is shown hereunder;



$$t\text{-BuO}\cdot \xrightarrow[k_1]{RH} t\text{-BuOH} + R\cdot \qquad t\text{-BuO}\cdot \xrightarrow[k_2]{} CH_3\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_3 + \cdot CH_3$$

From the mole ratio of the *t*-butyl alcohol and acetone obtained from the above reactions, it is possible to calculate the k_1/k_2 ratio. Although, in our experiments, the k_1/k_2 rate ratio cannot be given precisely because of the further reactions of *t*-butyl alcohol or acetone with *t*-butyl hypochlorite, for convenience it is permissible to adopt the mole ratio of *t*-butyl alcohol and acetone as a measure of the reactivity of the *t*-butoxy radical.

Recently, Russel has investigated particularly the solvent effects in the decomposition of di-*t*-butyl peroxide in the presence of cyclohexane at 130°C,[9] he has shown that such aromatic solvents as benzene caused a decrease in the k_1/k_2 rate ratio due to the high dissociation of the aromatic hydrocarbon-*t*-butoxy radical π-complex. Moreover, Walling has also pointed out that the aromatic solvents stabilize the transition state for β-scission through the contribution of the charge-transfer type structure, as is shown below:[10]



Concerning the solvent effects, however, the dilution effect with a solvent must also be taken into consideration, because the hydrogen abstraction reaction by the *t*-butoxy radical is proportional to the concentration of the *t*-butoxy radical and RH. The β-scission becomes preferential in the presence of a solvent as a result of this dilution effect. This effect is summarized in Table VII.

TABLE VII. DILUTION EFFECT

Exp. No.	C_6H_6/*t*-BuOCl Mole ratio	R[*1,*2] Mole ratio
11	10	0.83
a[*3]	5	1.14
b[*3]	14	0.7

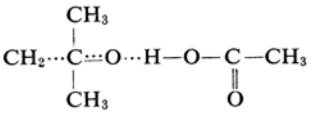
[*1] $R = \dfrac{(t\text{-BuOH} + \text{chloro-}t\text{-BuOH})}{(\text{acetone} + \text{monochloroacetone})}$

[*2] The value of R may be influenced by reaction temperature, but we considered that there was no great difference of R values within the range of 30°C to 40°C.

[*3] C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6111 (1960).

The mole ratio (R) of *t*-butyl alcohol and acetone decreases in proportion as the mole ratio of benzene and *t*-butyl hypochlorite increases. The R ratio in this experiment is summarized in Table VIII.

In the case of propionic acid, the R ratio is smaller than unity in the presence of benzene. In the reactions with monochloro- and trichloroacetic acids, R is always smaller than unity. In the case of acetic acid, however, R is, contrariwise, larger when the solvent is present than when there is no solvent. These results suggest that, as Walling has also described,[10] hydrogen bonding between the *t*-butoxy radical and acetic acid stabilizes the transition state of the β-scission.



In the case of propionic acid, however, this hydrogen bonding may be fairly unstable, the *t*-butoxy radical preferentially abstracts a hydrogen from the acid, and in the presence of the solvent, the β-scission of the radical proceeds predominantly as a results of the dilution effect.

The Reactivities of the *t*-Butoxy Radical.—Russell investigated the solvent effects in the photochlorination of hydrocarbons by molecular chlorine and found that, in the presence of some aromatic solvents, the chloro radical attacked hydrocarbons with a high selectivity.[11] Consequently, he considered that the selectivity may be ascribed to the formation of a π-complex between the chloro radical and the aromatic nucleus, and that this complex was less reactive and, therefore, more selective

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[9] G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959).

[10] C. Walling, *J. Am. Chem. Soc.*, **85**, 2333 (1963).

[11] a) G. A. Russell, ibid., **80**, 4987 (1958); b) G. A. Russell, ibid., **80**, 4997 (1958); c) G. A. Russell, ibid., **80**, 5002 (1958).

TABLE VIII. MOLE RATIO (R) OF t-BUTYL ALCOHOL AND ACETONE AT 30°C

Exp. No.	Carboxylic acid	Solvent	Solvent/tBuOCl Mole ratio	R*
1	CH_3COOH	None	—	0.21
2	CH_3COOH	None	—	0.33
3	CH_3COOH	C_6H_6	10	0.62
4	CH_3COOH	CCl_4	10	0.89
5	C_2H_5COOH	None	—	1.79
6	C_2H_5COOH	C_6H_6	10	0.8
7	n-C_3H_7COOH	None	—	1.69
8	$CH_2ClCOOH$	C_6H_6	10	0.77
10	CCl_3COOH	CCl_4	5	0.44
11	None	C_6H_6	10	0.83

* Considering further chlorinations of acetone and t-butyl alcohol, R was corrected as follows.

$$R = M_a/M_d$$

$M_a = t$-BuOH + Chloro-t-BuOH (mol.)
$M_d =$ Acetone + Monochloroacetone (mol.)

TABLE IX. ISOMER DISTRIBUTIONS — COMPARISON WITH OTHER DATA

RCOOH	Method	α-Isomer %	β-Isomer %	γ-Isomer %	Ref.
C_2H_5-	t-BuOCl + hν	61.2	38.8	—	
C_2H_5-	SO_2Cl_2 + B. P. O.	45	55	—	a)
n-C_3H_7-	t-BuOCl + hν	20.6	46.4	33.0	
n-C_3H_7-	SO_2Cl_2 + B. P. O.	10	45	45	a)
n-C_3H_7-	Cl_2 + hν	5	64	31	b)
n-C_3H_7-	Cl_2 + γ-ray	6	61	33	c)

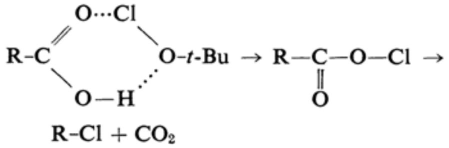
a) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 926 (1940).
b) A. Bruylants, M. Tits, C. Dieu and R. Gauthier, *Bull. soc. chim. Belges*, **61**, 266 (1952).
c) I. Rosen and J. P. Stallings, *Ind. Eng. Chem.*, **50**, 1512 (1958).

than the free chloro radical. On the other hand, Walling and his co-workers studied the similar chlorination by t-butyl hypochlorite.[1-3] They indicated that, even in the presence of an aromatic solvent, there was no change in the selectivitity of the t-butoxy radical as to the hydrogen abstraction. In our study of the chlorination of propionic acid as is shown in Table IV, the ratio of the α- and, β-isomers was constant, regardless of the presence or absence of benzene. These facts suggest that the t-butoxy radical does not form a π-complex with the aromatic solvent because of the small electron affinity and the bulkiness of the t-butoxy radical.

Now we will discuss in more detail the selectivity of the t-butoxy radical in the hydrogen abstraction from the carboxylic acids. For this purpose, our data are compared with other data and the results summarized in Table IX.

Propionic acid was chlorinated somewhat predominantly in the α-position in our study, but, on the contrary, in the β-position in Kharasch's experiment. On the other hand, chlorinations of n-butyric acid by all the methods listed in Table IX show a similar trend for the β-isomer to be formed most preferentially, followed by the γ-isomer. In our method, however, the formation of the α-isomer increased to some extent as compared with the other methods. From these results, we would conclude that the direction of the hydrogen abstraction by a radical with a large electron affinity, such as the chloro radical, is greatly influenced by the electron density on the carbon atoms of the alkyl group (the values of 88 kcal./mol. was determined for the electron affinity of the chloro radical). Thus, the α-position of propionic or n-butyric acid becomes inactive as a result of the electron-withdrawing effect of the carboxyl group. In n-butyric acid, the β-position is most reactive for the following two reasons. First, the inductive effect of the carboxyl group may be not so effective in the β-position as in the α-position. Second, the hyperconjugation of the methyl group makes a contribution to the β-position. For these two reasons, the electron density on the carbon atoms of the alkyl group becomes greatest in the β-position; therefore, this position may be easily attacked by a highly-electrophilic chloro radical. On the other hand, the electron affinity of the *t*-butoxy radical is not so high as the chloro radical (it is known that the electron affinity of the alkoxy radical is about 50 kcal./mol.) and, therefore, the electron density is not so effective in controlling the direction of the hydrogen abstraction from the alkyl group of the carboxylic acid by the *t*-butoxy radical. Consequently, *t*-butyl hypochlorite chlorinates *n*-butyric acid without selectivity, and the α-isomers increase in number in the chlorination of propionic acid by *t*-butyl hypochlorite.

Although Walling has recently reported that the formation of carbon dioxide was not detected in the reaction of *t*-butyl hypochlorite in acetic acid,[12] the formation of carbon dioxide was observed in our study. The decarboxylation of the carboxylic acids may proceed through the formation of acyl hypochlorite, followed by decomposition to give carbon dioxide and the corresponding alkyl chloride, as is shown below:



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