bath, 0.20 mm) to give 0.091 g of residual yellow oil. This was dissolved in a mixture of 5.0 ml of acetone and 1.0 ml of methyl iodide, 0.0438 g of anhydrous K_2CO_3 was added, and the mixture was heated at reflux for 3 hr. After cooling, the mixture was diluted with 15 ml of ether and filtered. Removal of solvent *in vacuo* then afforded 0.094 g of yellow oil which showed infrared absorption at 1734, 1716, 1652, and 1607 cm^{-1}.

Registry No.—**2b**, 36873-61-7; **2d**, 36873-62-8; **3a**, 36873-63-9; **3b**, 36873-64-0; **4b**, 36873-65-1; **4b** dinitrophenylhydrazone, 36873-66-2; **6a**, 36873-67-3; **6b**, 36873-68-4; **7a**, 36873-69-5; **7b**, 36873-70-8; **13**, 36873-71-9; **14**, 36873-72-0; **15**, 36873-73-1; **17**, 36873-74-2; **20b**, 36873-75-3; **21**, 36873-76-4.

Mechanism for the Peracetic Acid Oxidation of *trans*-α-Iodo-α′-acetoxystilbene to Benzil[1]

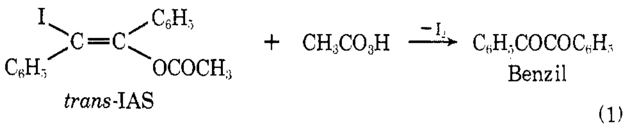
YOSHIRO OGATA* AND IWAO URASAKI

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

Received June 19, 1972

The mechanism for the reaction of *trans*-α-iodo-α′-acetoxystilbene (*trans*-IAS) with peracetic acid to form benzil has been studied by means of its kinetics and the examination of related reactions. The rate is expressed as $v = (k_2 + k_2'h_0)[trans\text{-IAS}][CH_3CO_3H]$. The reaction is accelerated in a more acidic solvent, but it is retarded by addition of sodium acetate and stopped in strongly basic solvents. *trans*- and *cis*-α,α′-diacetoxystilbene (DAS) are stable against peracetic acid alone, but they are oxidized to benzil by a mixture of peracetic acid and iodine or alkyl iodide. *trans*-IAS gives on treatment with peracetic acid in the presence of anisole *trans*-DAS, benzoin and its acetate together with other products. The reaction of *trans*-α,α′-diiodostilbene (*trans*-DIS) with peracetic acid in propionic acid gives *trans*-α-iodo-α′-propionyloxystilbene (*trans*-IPS) by introduction of solvent carboxylate group. These results suggest a mechanism involving a rate-determining electrophilic attack by peracetic acid on the iodine atom of IAS to give vinylic cation, which yields DAS by the reaction with solvent acetic acid. Then DAS reacts with produced acetyl hypoiodite, the adduct being further oxidized and hydrolyzed to give benzil.

In our previous paper,[2] we reported that *trans*-α-iodo-α′-acetoxystilbene (*trans*-IAS), a product by iodoacetoxylation of tolan, gave benzil on oxidation with peracetic acid (eq 1). The mechanism of this reaction



trans-IAS

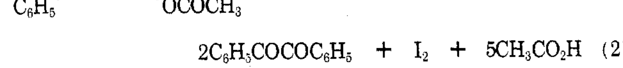
(1)

is of interest in comparison to the solvolysis of vinyl halides, since a vinyl cation may be an intermediate in the oxidation. There are many examples of solvolysis of a vinyl halide involving an intermediary vinyl cation.[3-7] Thus, acetolyses of both *cis*- and *trans*-1-iodo-1-cyclopropylpropenes in the presence of silver acetate at 25° gave equal amounts of stereoisomeric acetates as major products, pointing to the conclusion that the products arising from both cis and trans iodides are formed from the same intermediate, which is most likely a linear vinyl cation.[7] The calculations on 1-cyclopropylvinyl cations by means of the extended Hückel molecular orbital method also suggest that the ions are most stable in the linear, bisected conformation.[8]

There are some obscurities in the mechanism for oxidation of *trans*-IAS to benzil (eq 1). (1) Where is the initial attacking site of peracid? (2) Is the attacking species an electrophile? (3) Is a vinyl cation involved? (4) Is α,α′-diacetoxystilbene (DAS) an intermediate in analogy with the formation of IAS from *trans*-α,α′-diiodostilbene (*trans*-DIS)? For the elucidation of these questions, we carried out the kinetic studies and then examined the related reactions, *i.e.*, oxidations of DAS and DIS with peracetic acid in the presence or absence of iodine or alkyl iodide. Further, we attempted to detect a hypothetical intermediate, DAS. The present paper describes a probable mechanism for the oxidation of *trans*-IAS with peracetic acid as well as of related reactions.

Results and Discussion

Stoichiometry.—The reaction of *trans*-IAS with peracetic acid gives benzil together with iodine.[2] Since the main products are benzil (based on tlc analysis) and iodine, the stoichiometry may be as follows.



$$2C_6H_5COCOC_6H_5 + I_2 + 5CH_3CO_2H \quad (2)$$

However, it must be taken into account that peracetic acid is consumed also by the further oxidation of iodine and/or hypoiodous acid probably present in the reaction mixture, and by the decomposition of peracid itself. Hence, for the examination of the stoichiometry, the conversion of IAS to benzil, the consumption of peracetic acid, and the formation of iodine should be studied simultaneously at appropriate time intervals. Figure 1 shows conversion curves, which indicate that more than 2 mol of peracetic acid is consumed and less than 0.5 mol of iodine is formed by consuming 1 mol of IAS (or by formation of benzil). This result means that more than 0.5 mol of peracetic acid is consumed by further oxidation of iodine compounds or by decomposition.

---

[1] Contribution No. 185.

[2] Y. Ogata and I. Urasaki, *J. Org. Chem.*, **36**, 2164 (1971).

[3] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964).

[4] L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, **90**, 7282 (1968); Z. Rappoport and A. Gal, *ibid.*, **91**, 5246 (1969); Z. Rappoport and Y. Apeloig, *ibid.*, **91**, 6734 (1969).

[5] S. J. Huang and M. V. Lessard, *ibid.*, **90**, 2432 (1968).

[6] S. A. Sherrod and R. G. Bergman, *ibid.*, **91**, 2115 (1969); **93**, 1925 (1971); T. C. Clarke, D. R. Kilsey, and R. G. Bergman, *ibid.*, **94**, 3626 (1972); M. Hanack and T. Bässler, *ibid.*, **91**, 2117 (1969).

[7] D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970); **93**, 1941 (1971).

[8] D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1953 (1971).

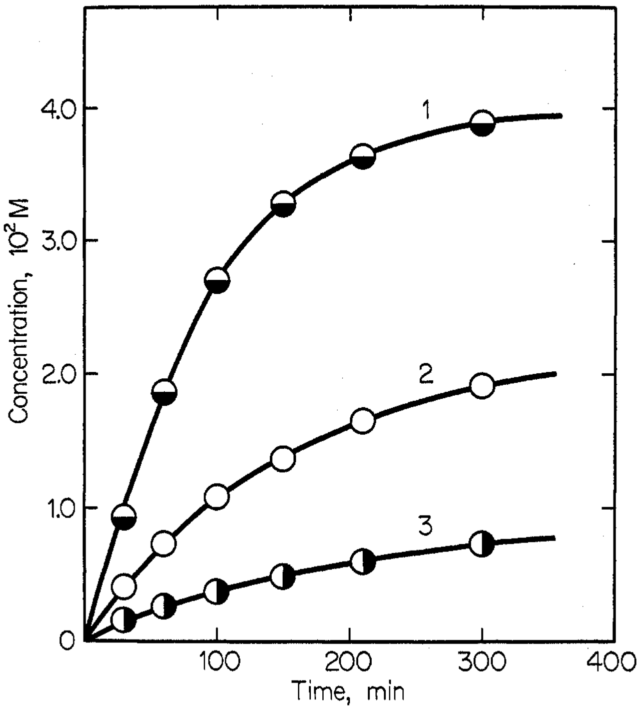


Figure 1.—Stoichiometric examination for the reaction of *trans*-IAS with peracetic acid in acetic acid at 50°. Initial concentration: [IAS] = 0.040 *M*, [CH_3CO_3H] = 0.060 *M*. 1, consumption of peracetic acid; 2, consumption of IAS or formation of benzil; 3, formation of iodine.

Rate Law.—Because of the excess consumption of peracetic acid as stated above, the rate of the consumption of peracetic acid is complicated. Therefore, the rate of the conversion of *trans*-IAS to benzil with excess peracetic acid was measured by means of uv spectrophotometry, and the obtained pseudo-first-order rate constants at 50° are listed in Table I. The plots of log k_1 *vs.* log [CH_3CO_3H] gave a straight line with a slope of 0.98 and an intercept of −3.01. Hence, the rate law is expressed as eq 3.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF *trans*-IAS WITH PERACETIC ACID IN ACETIC ACID AT 50°

Initial concn, *M*			
[IAS]	[CH_3CO_3H]	Added iodine, *M*	$10^5 k_1$, sec^{-1}
0.005	0.10		10.4
0.010	0.10		9.3
0.015	0.10		10.1
0.020	0.10		9.0
0.010	0.05		5.3
0.010	0.15		15.3
0.010	0.20		18.9
0.010	0.10	0.005	9.9
0.010	0.10	0.010	10.4

$$v = k_2[trans\text{-IAS}][CH_3CO_3H] \tag{3}$$

Here k_2 was calculated to be 9.7×10^{-4} M^{-1} sec^{-1}. The rate is nearly equal to that of the reaction of iodine with peracetic acid (1.25×10^{-3} M^{-1} sec^{-1} at 50°).[9] As shown in Table I, the rate is not affected by addition of iodine.

Effect of Sulfuric Acid.—As shown in Table II, the addition of sulfuric acid increases the rate, and the plots of log ($k_1 - k_0$) *vs.* Hammett's acidity function (H_0)[10] gave a straight line with a slope of −0.99 as indicated in Figure 2. Thus, the rate is expressed as eq 4, where k_2 and k_2' represent uncatalyzed and acid-catalyzed oxidations, respectively.

$$v = (k_2 + k_2'h_0)[trans\text{-IAS}][CH_3CO_3H] \tag{4}$$

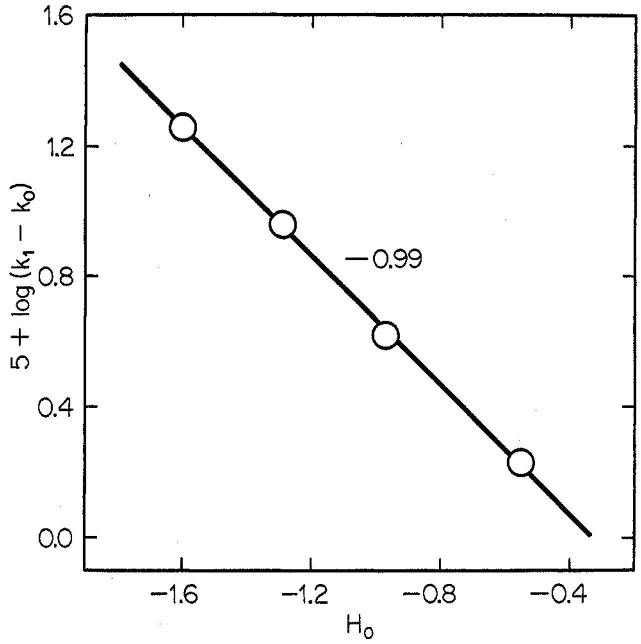


Figure 2.—Plots of log ($k_1 - k_0$) *vs.* H_0 for the reaction of *trans*-IAS with peracetic acid in acetic acid at 50°. Initial concentration: [IAS] = 0.010 *M*, [CH_3CO_3H] = 0.10 *M*.

TABLE II

EFFECT OF ADDED SULFURIC ACID ON THE REACTION OF *trans*-IAS WITH PERACETIC ACID IN ACETIC ACID AT 50° [a]

[H_2SO_4], *M*	H_0[10]	$10^5 k_1$, sec^{-1}	$10^5(k_1 - k_0)$, sec^{-1}	5 + log ($k_1 - k_0$)
0		9.3 (= k_0)[b]		
0.010	−0.55	11.0	1.7	0.23
0.025	−0.97	13.5	4.2	0.62
0.050	−1.29	18.5	9.2	0.96
0.100	−1.60	27.7	18.4	1.26

[a] Initial concentration: [IAS] = 0.010 *M*, [CH_3CO_3H] = 0.10 *M*. [b] k_0 is obtained by extrapolation of k_1 to [H_2SO_4] = 0.

Effect of Sodium Acetate.—The addition of sodium acetate to an acetic acid solution of the reaction mixture decreased the rate, as shown in Table III. However, at higher concentration of sodium acetate, side reactions seem to occur, because fairly large amounts of unidentified products were formed on the basis of tlc analysis.

TABLE III

EFFECT OF SODIUM ACETATE ON THE REACTION OF *trans*-IAS WITH PERACETIC ACID IN ACETIC ACID AT 50°

Initial concn, *M*			
[IAS]	[CH_3CO_3H]	[CH_3CO_2Na]	$10^5 k_1$, sec^{-1}
0.010	0.10	0	9.3
0.010	0.10	0.005	3.6
0.010	0.10	0.010	1.9

Solvent Effect.—The yield of benzil in the reaction of *trans*-IAS with peracetic acid was determined at 50° in

---

[9] Y. Ogata and K. Nakajima, *Tetrahedron*, **20**, 43 (1964).

[10] N. F. Hall and W. F. Spengeman, *J. Amer. Chem. Soc.*, **62**, 2487 (1940).

various solvents. The results are listed in Table IV, indicating that the reaction is accelerated in a more acidic solvent except in chloroform and almost stops in basic solvents. The reactivity is independent of the dielectric constant of solvent. The fairly fast rate of reaction in chloroform may be an artifact due to the generation of hydrogen chloride from the solvent in a radical reaction. In fact, chloride ion was detected as silver chloride even by mixing of chloroform and peracetic acid alone under the same conditions. In view of these results as well as the effect of sulfuric acid, it may be said that the reaction is general acid catalyzed, suggesting the electrophilic nature of the attacking species. The appreciable rate enhancement in carbon tetrachloride may be due to a catalysis by acetic acid existing in peracetic acid. Basic solvents must annul this catalysis.

TABLE IV

SOLVENT EFFECT ON THE YIELD OF 3-HR REACTION OF *trans*-IAS WITH PERACETIC ACID AT 50° [a]

Solvent[b]	Dielectric constant	pK_a (25°)	Yield of benzil, %
Dioxane	2.21		~0
Ethanol	24.3		~0
Methanol	32.6	16	
Acetonitrile	37.5	25	~0
Carbon tetrachloride	2.24		13.4
85% Aqueous propionic acid			13.6
Propionic acid	3.44	4.87	17.3
85% Aqueous acetic acid			27.3
Acetic acid	6.15	4.76	35.4
Chloroform	4.81		44.5
85% Aqueous formic acid			50.6
Formic acid	58.5	3.74	

[a] Initial concentration: [IAS] = 0.020 *M*, [CH_3CO_3H] = 0.030*M*. [b] In all cases about 1.5% of acetic acid is also contained because the acetic acid solution of *ca.* 2 *M* peracetic acid was used.

Temperature Effect.—The rate of the reaction of *trans*-IAS with peracetic acid was measured in acetic acid at various temperatures with initial concentrations of IAS and peracetic acid of 0.01 and 0.10 *M*, respectively. The pseudo-first-order rate constants ($10^5\ k_1$, sec^{-1}) were 6.4 at 45°, 9.9 at 50°, 15.0 at 55°, and 23.0 at 60°. The plot of log k_1 *vs.* $1/T$ afforded a straight line, giving the values of 17.8 kcal mol^{-1} and -23.8 eu for the energy and entropy of activation, respectively.

Intermediacy of DAS.—The oxidation of *trans*-DIS with peracetic acid in acetic acid affords IAS as well as benzil.[2] Therefore, it is expected that DAS may be formed similarly as an intermediate in the reaction of *trans*-IAS with peracetic acid in acetic acid. However, no DAS was detected in the reaction mixture according to tlc analysis. Hence, if DAS is truely an intermediate, it must be oxidized to benzil rapidly under the reaction conditions. Thus, the reactivity of DAS under similar reaction conditions was investigated to examine the intermediacy of DAS.

Both *trans*- and *cis*-DAS are hardly oxidized with peracetic acid alone, but they are oxidized to benzil in the presence of iodine. Table V shows the results on the rate for *trans*-DAS with excess peracetic acid. As apparent from Table V, the rate law can be expressed as eq 5.

$$v = k_3[trans\text{-DAS}][I_2][CH_3CO_3H] \qquad (5)$$

TABLE V

EFFECT OF IODINE ON THE REACTION OF *trans*-DAS WITH PERACETIC ACID TO FORM BENZIL IN ACETIC ACID AT 50°

Initial concn, *M*			
[DAS]	[CH_3CO_3H]	[I_2]	$10^5\ k_1$, sec^{-1}
0.010	0.10	0	0
0.010	0.10	0.002	2.3
0.010	0.10	0.005	4.8
0.010	0.10	0.010	10.2
0.010	0.10	0.005	3.6[a]

[a] Reaction rate for *cis*-DAS.

Here, the value of k_3 is $1.02 \times 10^{-1}\ M^{-2}\ sec^{-1}$, which is a little smaller than the value for the oxidation of *trans*-IAS at 0.005 *M* iodine concentration. It can easily be seen that this rate behavior for the reaction of DAS with a mixture of iodine and peracetic acid is the general one for iodoacetoxylation of olefins,[11-13] though the rate is slow compared with that of propylene.[12] This slow rate may be due to the low electron density at the double bond of DAS by the conjugation with two phenyl groups, so that the π-complex formation between iodine and the double bond of DAS may be difficult.

Here, it seems likely that the original iodine compound formed in the reaction of IAS with peracetic acid is not a molecular iodine but an iodine compound like hypoiodous acid or acetyl hypoiodite. Consequently, it is necessary to examine the reaction of DAS with hypoiodous acid or acetyl hypoiodite.

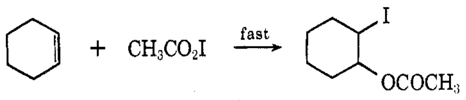
The reaction of alkyl iodides with peracetic acid in the presence of aromatic and olefinic compounds has been reported to give aromatic iodides[14] and iodoacetoxylated products,[13] respectively, where acetyl hypoiodite has been suggested to be an attacking species as shown in eq 6-9, because it is more electrophilic than

$$RI + CH_3CO_3H \xrightarrow{slow} HOI + CH_3CO_2R \qquad (6)$$

$$HOI + CH_3CO_2H \overset{fast}{\rightleftharpoons} CH_3CO_2I + H_2O \qquad (7)$$

$$ArH + CH_3CO_2I \xrightarrow{fast} ArI + CH_3CO_2H \qquad (8)$$

or



(9)

hypoiodous acid. Since the oxidation of alkyl iodide with peracetic acid is much (*ca.* 30 times with *n*-butyl iodide) faster than that of iodine,[14] the reaction of *trans*-DAS with peracetic acid in the presence of alkyl iodide was examined. The pseudo-first-order rate constants are listed in Table VI, which suggests

TABLE VI

EFFECT OF ALKYL IODIDES ON THE INITIAL RATE OF THE PERACETIC ACID OXIDATION OF *trans*-DAS TO FORM BENZIL IN ACETIC ACID AT 30° [a]

Iodide	Concn, *M*	$10^5\ k_1$, sec^{-1}
n-Butyl	0.010	3.7
n-Propyl	0.010	1.3
Isopropyl	0.010	0.40
Molecular iodine	0.005	0.24

[a] Initial concentration: [DAS] = 0.010 *M*, [CH_3CO_3H] = 0.10 *M*.

---

[11] Y. Ogata, K. Aoki, and Y. Furuya, *Chem. Ind. (London)*, 304 (1965).

[12] Y. Ogata and K. Aoki, *J. Org. Chem.*, **31**, 1625 (1966).

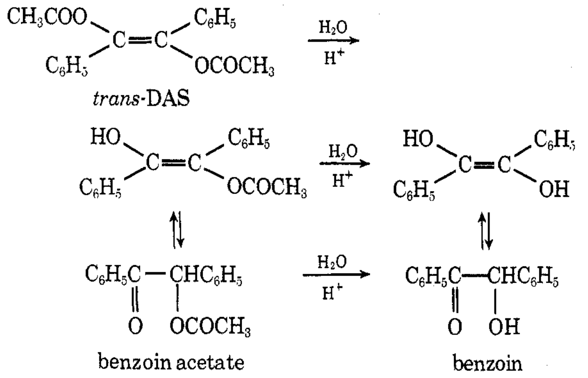
[13] Y. Ogata and K. Aoki, *ibid.*, **34**, 3978 (1969).

[14] Y. Ogata and K. Aoki, *ibid.*, **34**, 3974 (1969).

that DAS reacts considerably faster with acetyl hypoiodite to form benzil. This means that acetyl hypoiodite formed by the peracetic acid oxidation of IAS may react rapidly with DAS to form benzil, so that DAS cannot be detected in the reaction mixture irrespective of the intermediacy of DAS. Hence, it is probable that DAS is an intermediate in the present reaction. In this connection, the addition of acetyl hypoiodite to IAS seems to be difficult because of the steric hindrance.

Attempted Detection of DAS.—If DAS is truely an intermediate in the peracetic acid oxidation of IAS, then it may be detected by trapping acetyl hypoiodite with electron-rich compounds such as *m*-xylene or anisole which can easily react with acetyl hypoiodite.[15]

Although DAS could not be detected in the presence of *m*-xylene by means of tlc, the products in the presence of anisole gave tlc spots identical with those of benzoin, benzoin acetate, and *trans*-DAS as well as several other unidentified products which may be iodinated or oxidized anisoles.[15,16] It is interesting that benzil could not be detected from the reaction mixture by the tlc analysis. These results also support the intermediacy of DAS, though there still remains some uncertainty in the tlc analysis. The formation of benzoin and its acetate may be due to the hydrolysis of DAS followed by keto–enol tautomerization (eq 10). The fact that no *cis*-DAS could be detected is probably due to the steric interaction between two phenyl groups, but the possibility of the formation of a little *cis*-DAS cannot be denied.

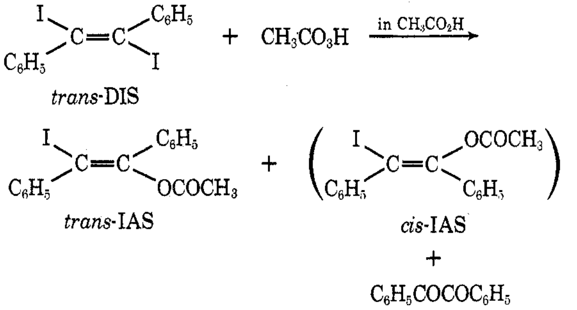


(10)

Benzoin and its acetate are also detected from the reaction of *trans*-IAS with peracetic acid in the presence of sulfuric acid (*ca.* 0.5 *M*), which also suggests the intermediacy of DAS, for the hydrolysis of DAS to form benzoin acetate or benzoin may be catalyzed by sulfuric acid, so that hydrolysis of DAS becomes competitive with the reaction of DAS with acetyl hypoiodite at high concentration of sulfuric acid. Besides, benzoin and particularly its acetate are found to be fairly stable under these conditions.

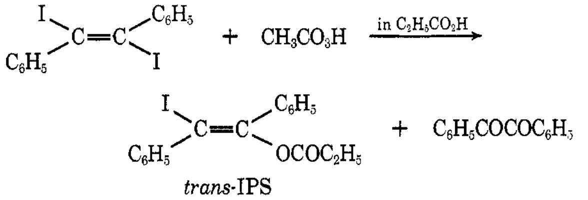
Peracid Oxidation of DIS.—The above discussion shows that DAS may be an intermediate in the reaction of *trans*-IAS with peracetic acid. The next questions are the stereochemistry of the DAS formation and the intermediacy of a vinyl cation. The DAS formed consisted mostly of trans isomer on the basis of tlc analysis. Here, the analogous reaction of *trans*-DIS with peracetic acid was examined as described below, because the intermediate IAS can easily be isolated from the reaction mixture.

Firstly, more detailed examination of the reaction of DIS with peracetic acid in acetic acid showed the formation of *cis*-α-iodo-α′-acetoxystilbene (*cis*-IAS) as well as the trans isomer and benzil, though the amount of *cis*-IAS was very small (eq 11). Thus, the IAS fraction, which was isolated by column chromatography of the products, showed a melting point lower than that of pure *trans*-IAS, and its nmr spectrum gave another small singlet signal at τ 7.77 in addition to a singlet signal of the acetoxyl proton of *trans*-IAS at τ 8.21. The signal at τ 7.77 may correspond to the acetoxyl proton of *cis*-IAS, because it is very close to the signal of the acetoxyl proton of *cis*-α-bromo-α′-acetoxystilbene (τ 7.79).[17]



(11)

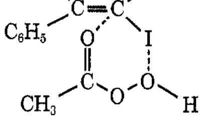
The reaction of DIS with peracetic acid in propionic acid gave *trans*-α-iodo-α′-propionyloxystilbene (*trans*-IPS) (identified by ir and nmr spectra and elemental analysis) and benzil (eq 12), and virtually no IAS (tlc) or *cis*-IPS (nmr) was detected. Further, the reaction of DIS with peracetic acid in a mixture of equal volumes of acetic and propionic acids gave nearly equal amounts of IAS and IPS (tlc).

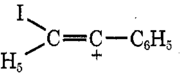


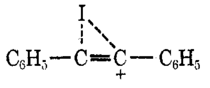
(12)

In the above reactions, the catalytic amount of sulfuric acid (*ca.* 10^{-3} *M*) contained in the solution was preliminarily neutralized with an equivalent amount of sodium acetate to prevent the transfer of an active oxygen from peracetic acid to propionic acid. In fact, the transfer of an active oxygen from peracetic acid to hexahydrobenzoic acid was prevented by the addition of sodium acetate equivalent to the sulfuric acid contained. Otherwise, the active oxygen was transferred a little, the second-order rate constant being *ca.* $6 \times 10^{-7}\ M^{-1}\ \text{sec}^{-1}$ at 50° in the presence of $3.9 \times 10^{-3} M$ sulfuric acid.

Therefore, for the formation of IAS by peracid oxidation of DIS, the acetoxyl group of IAS does not come from peracid, but from the solvent, acetic acid. Hence, a cyclic transition state such as I is improbable, but a


I


II


III

---

[15] Y. Ogata and K. Aoki, *J. Amer. Chem. Soc.*, **90**, 6187 (1968).

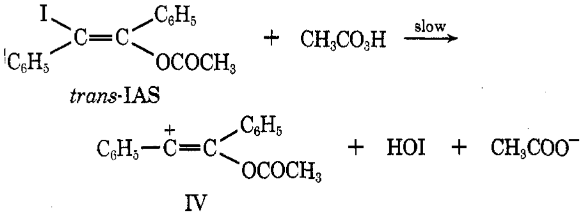
[16] J. Böeseken and C. F. Metz, *Recl. Trav. Chim. Pays-Bas*, **54**, 345 (1935).

[17] A. Jovtscheff and S. L. Spassov, *Monatsh. Chem.*, **98**, 2272 (1967).

vinyl cation, II, or a cyclic one, III, may be formed by the oxidative elimination of idodide ion from DIS with peracetic acid. Assuming III, a preferential formation of *trans*-IAS can be understood; such a cyclic vinyl cation was also proposed for β-thiovinyl cations.[18] Of course, the steric interaction between two phenyl groups is also expected to cause a little formation of *cis*-IAS, as described for the formation of DAS from IAS.

Oxidation Mechanism for IAS.—All of the above findings suggest the following mechanism for the peracetic acid oxidation of *trans*-IAS to form benzil, which is similar to that of DIS. The effects of sulfuric acid, sodium acetate, and solvent imply that the reaction proceeds with an electrophilic attack by peracetic acid, but no nucleophilic attack by peracetate ion, which is also supported by the fact that *trans*-IAS is stable even on 5-hr refluxing with sodium acetate in acetic acid. The nucleophilic substitution at a vinylic carbon is known to be difficult.[8]

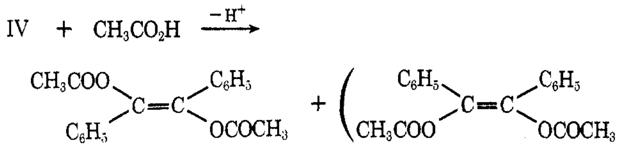
Thus the rate-determining electrophilic attack by peracetic acid on IAS allows the oxidative abstraction of iodide ion from IAS to form hypoiodous acid and a vinyl cation, IV (eq 13), where peracetic acid is activated by hydrogen bonding of solvent acetic acid to the carbonyl group of peracetic acid and activated more effectively by the protonation of peracetic acid with mineral acids. A rapid nucleophilic attack by solvent acetic acid on IV yields DAS, most of which is expected to be trans isomer (eq 14). Furthermore, DAS is subject to the rapid electrophilic addition of acetyl hypoiodite which is formed from hypoiodous acid with acetic acid (eq 7), to give the adduct V (eq 15), followed by the further oxidation with peracetic acid to provide α,α'-tetraacetoxybibenzyl, VI (eq 16), which may easily be hydrolyzed with water[19] yielding benzil (eq 17). Oxidation of V with peracetic acid forming VI may involve a carbonium ion VII (eq 18).



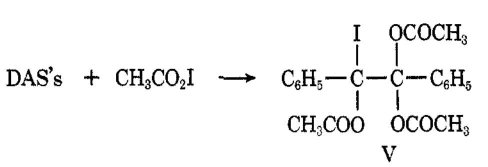
trans-IAS

IV

(13)

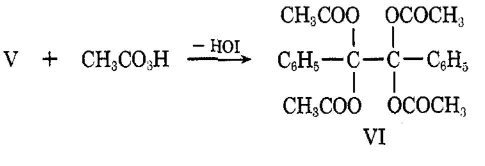


trans-DAS *cis*-DAS (14)



$$\text{DAS's} + CH_3CO_2I \longrightarrow C_6H_5-\underset{CH_3COO}{\overset{I}{C}}-\underset{OCOCH_3}{\overset{OCOCH_3}{C}}-C_6H_5 \quad (15)$$

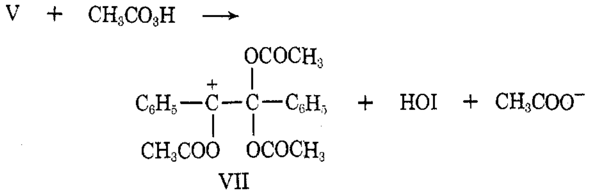
V



$$V + CH_3CO_3H \xrightarrow{-\,HOI} C_6H_5-\underset{CH_3COO}{\overset{CH_3COO}{C}}-\underset{OCOCH_3}{\overset{OCOCH_3}{C}}-C_6H_5 \quad (16)$$

VI

$$VI + 2H_2O \longrightarrow C_6H_5COCOC_6H_5 + 4CH_3CO_2H \quad (17)$$



$$V + CH_3CO_3H \longrightarrow C_6H_5-\underset{CH_3COO}{\overset{+}{C}}-\underset{OCOCH_3}{\overset{OCOCH_3}{C}}-C_6H_5 + HOI + CH_3COO^- \quad (18)$$

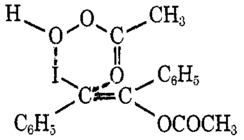
VII

Since acetyl hypoiodite is a good electrophile, its attack on V or even on IAS is expected to give VII or IV accompanied by the formation of molecular iodine (eq 19 and 20).

$$V + CH_3CO_2I \longrightarrow VII + I_2 + CH_3COO^- \quad (19)$$

$$IAS + CH_3CO_2I \longrightarrow IV + I_2 + CH_3COO^- \quad (20)$$

In analogy with the formation of IPS in the peracetic acid oxidation of DIS in propionic acid, which excludes a cyclic transition state I, the reaction of IAS may also deny a cyclic one VIII.



VIII

The mechanism described above agrees with the stoichiometry as indicated below. (a) When reaction 19 alone is considered for the formation of iodine, the following steps are probable.

$$2\ trans\text{-IAS} + 2CH_3CO_3H \longrightarrow$$

$$2IV + 2HOI + 2CH_3COO^- \quad (13)$$

$$2IV + 2CH_3CO_2H \longrightarrow 2DAS + 2H^+ \quad (14)$$

$$2HOI + 2CH_3CO_2H \rightleftharpoons 2CH_3CO_2I + 2H_2O \quad (7)$$

$$2DAS + 2CH_3CO_2I \longrightarrow 2V \quad (15)$$

$$V + CH_3CO_3H \longrightarrow VII + HOI + CH_3COO^- \quad (18)$$

$$HOI + CH_3CO_2H \rightleftharpoons CH_3CO_2I + H_2O \quad (7)$$

$$V + CH_3CO_2I \longrightarrow VII + I_2 + CH_3COO^- \quad (19)$$

$$2VII + 2CH_3CO_2H \longrightarrow 2VI + 2H^+ \quad (21)$$

$$2VI + 4H_2O \longrightarrow 2C_6H_5COCOC_6H_5 + 8CH_3CO_2H \quad (17)$$

$$4H^+ + 4CH_3COO^- \longrightarrow 4CH_3CO_2H \quad (22)$$

Summing up leads to eq 2, which is the stoichiometry described above. (b) When reaction 20 alone is considered for the formation of iodine, the following steps are possible.

$$trans\text{-IAS} + CH_3CO_3H \longrightarrow IV + HOI + CH_3COO^- \quad (13)$$

$$IV + CH_3CO_2H \longrightarrow DAS + H^+ \quad (14)$$

$$HOI + CH_3CO_2H \rightleftharpoons CH_3CO_2I + H_2O \quad (7)$$

$$DAS + CH_3CO_2I \longrightarrow V \quad (15)$$

$$V + CH_3CO_3H \longrightarrow VII + HOI + CH_3COO^- \quad (18)$$

$$HOI + CH_3CO_2H \rightleftharpoons CH_3CO_2I + H_2O \quad (7)$$

$$trans\text{-IAS} + CH_3CO_2I \longrightarrow IV + I_2 + CH_3COO^- \quad (20)$$

$$IV + CH_3CO_2H \longrightarrow DAS + H^+ \quad (14)$$

$$DAS + CH_3CO_2I \longrightarrow V \quad (15)$$

$$V + CH_3CO_3H \longrightarrow VII + HOI + CH_3COO^- \quad (18)$$

$$HOI + CH_3CO_2H \rightleftharpoons CH_3CO_2I + H_2O \quad (7)$$

---

[18] G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, *Chem. Commun.*, 1520 (1969); G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc. C*, 2625 (1970).

[19] J. Jovtscheff and S. L. Spassov, *Monatsh. Chem.*, **98**, 2326 (1967).

$$2\text{VII} + 2CH_3CO_2H \longrightarrow 2\text{VI} + 2H^+ \qquad (21)$$

$$2\text{VI} + 4H_2O \longrightarrow 2C_6H_5COCOC_6H_5 + 8CH_3CO_2H \qquad (17)$$

$$4H^+ + 4CH_3COO^- \longrightarrow 4CH_3CO_2H \qquad (22)$$

The total equation is the same (eq 2) as that in a, indicating that the mechanism should agree with the stoichiometry whatever the ratio of reaction 19 to 20 may be.

Experimental Section

Materials.—*Ca.* 2.5 *M* peracetic acid in acetic acid was used, which was prepared by the reaction of acetic anhydride with 60% H_2O_2 in the presence of a catalytic amount of H_2SO_4.[20] The concentration of H_2SO_4 in the solution was about 0.039 *M*. *trans*-IAS was prepared by the reaction of tolan with a mixture of iodine and peracetic acid in acetic acid,[2] yield 59%, mp 146–146.5° (from methanol) (lit.[2] mp 146–146.5). *trans*-DIS was prepared by the addition of iodine to tolan in acetic acid at room temperature under irradiation of light for 4 hr, yield 88%, mp 191° dec in a sealed tube (lit.[21] mp 199° dec). DAS (a mixture of cis and trans isomers) was prepared by the reductive acetylation of benzil with zinc dust and acetic anhydride in the presence of sulfuric acid.[22] *trans*-DAS was purified by fractional crystallization and recrystallized from methanol, mp 157° (lit.[22] mp 155°). *cis*-DAS was separated by chromatography on silica gel in benzene–chloroform–ethyl acetate (20:2:1), and recrystallized from ligroin, mp 119.5° (lit.[22] mp 119°). Benzoin acetate was prepared by the acetylation of benzoin with acetic anhydride,[23] mp 82° (from ethanol) (lit.[23] mp 81.5–82.5°). Alkyl iodides were prepared by refluxing respective alcohols with a mixture of iodine and red phosphorus:[24] *n*-propyl, bp 101.7–102.3°; isopropyl, bp 88.7–89.0°; and *n*-butyl iodide, bp 63° (80 mm). Acetic acid used as a solvent for kinetic study was purified by rectification, bp 118–119°. All the other commercial solvents were used without further purification.

Product Analyses.—Products were analyzed by means of tlc using a 200 × 200 mm plate dragged with silica gel G according to Stahl ∼ 0.3 mm thick. The R_f values of various compounds for several developing solvents are listed in Table VII.

TABLE VII

R_f VALUES ON TLC USING SILICA GEL *ca.* 0.3 MM THICK

Compd	Developing solvents		
	Benzene	Benzene–ethyl acetate (20:1)	Benzene–chloroform–ethyl acetate (20:2:1)
Tolan	0.87	0.88	
trans-IPS	0.74		
trans-IAS	0.69	0.72	
Benzil	0.64	0.67	0.73
trans-DAS	0.42	0.51	0.58
Benzoin acetate		0.47	
cis-DAS	0.34	0.43	0.46
Benzoin		0.34	0.38

Procedure for Stoichiometric Examination.—The conversion of *trans*-IAS to benzil and the consumption of peracetic acid along with the formation of iodine were measured simultaneously by uv spectroscopy and by iodometric titration, respectively. Separate acetic acid solutions of IAS and peracetic acid were mixed at 50° to start the reaction, giving the solution of 0.04 *M* IAS and 0.06 *M* peracetic acid. Aliquots (each 2 ml) were pipetted out at appropriate intervals of time and poured into a separatory funnel containing CCl_4 (15 ml) and water (40 ml), the funnel being shaken rapidly to extract iodine. After one more extraction (5 ml), the combined extracts were washed with water and separated. The content of iodine in CCl_4 and that of peracetic acid in the combined aqueous layer were measured iodometrically with 0.01 *N* thiosulfate solution. The titrated CCl_4 layer was then washed with water and dried (Na_2SO_4). After CCl_4 was removed, the residue was then dissolved in methanol, and the composition between IAS and benzil was measured by means of uv spectrophotometry.

Ultraviolet Spectrophotometry.—Methanolic solutions containing known concentrations of *trans*-IAS and benzil were prepared, and extinctions at 230 and 260 mμ were measured by a Hitachi double-beam spectrophotometer, Model 124. The compositions calculated from the extinctions and molecular absorption coefficient of each component agreed with the theoretical within 1% error. Hence, the component of the reaction mixture can be measured by uv spectrophotometry, since the only main product is benzil.

When the composition between *trans*-DAS and benzil was measured, the extinctions at 250 and 280 mμ were used, and the extinctions at 258 and 290 mμ were used for the measurement of the composition between *cis*-DAS and benzil.

Typical Procedure for the Rate Measurements.—The rate of the conversion of *trans*-IAS to benzil under the existence of excess peracetic acid was measured by means of uv spectrophotometry. A 0.02 *M* acetic acid solution of IAS (5 ml) and acetic acid (4.55 ml) were mixed in a sample tube and allowed to stand at 50° to reach temperature equilibrium. Another solution (0.45 ml) of 2.25 *M* peracetic acid in acetic acid at 50° was added quickly to the above solution to start the reaction, giving the solution of 0.01 *M* IAS and 0.10 *M* peracetic acid. Aliquots (each 1 ml) were pipetted out at known intervals of time and placed in a separatory funnel containing CCl_4 (5 ml), water (5 ml), K_2CO_3 (1.4 g), and KI (0.15 g) to liberate I_2. Aqueous 0.2 *N* $Na_2S_2O_3$ (2 ml) was then added to the funnel. The funnel was shaken and the two layers were separated. The CCl_4 layer was dried (Na_2SO_4), an aliquot (0.2 ml) was pipetted out, CCl_4 was removed under reduced pressure, the residue was dissolved in methanol (7–8 ml), and then the composition between IAS and benzil was measured by means of uv spectrophotometry. The reactions were usually followed until 30–60% conversion was attained. The rate of the reaction of *trans*- or *cis*-DAS with a mixture of iodine and peracetic acid to form benzil was measured by the same method.

Reaction of DAS with Peracetic Acid in the Presence or Absence of Iodine.—An acetic acid solution (5 ml) of DAS (0.05 *M*), peracetic acid (0.05 *M*), and iodine (0.01 *M*) was kept standing at 70° for 3 hr. The reaction mixture was diluted with water and extracted with ether. The extract was treated successively with aqueous KI, $Na_2S_2O_3$, and $NaHCO_3$, and washed with water. The mixture was analyzed by means of tlc in benzene, giving two spots corresponding to DAS and benzil. The yield of benzil was 29% from *trans*-DAS and 24% for the cis isomer (spectrophotometry).

When the same reaction of DAS was carried out in the absence of iodine, the reaction gave only recovered DAS.

Oxidation of IAS in the Presence of Anisole.—The solution of *trans*-IAS (0.04 *M*) and peracetic acid (0.04 *M*) in the mixture of acetic acid (1 ml) and anisole (1 ml) was kept standing at 50° for 3 hr. The reaction mixture was diluted with water, being neutralized with K_2CO_3, and extracted with CCl_4. CCl_4 and most of anisole were removed from the dried (Na_2SO_4) extract under reduced pressure, giving a yellow liquid. The analysis on tlc in benzene–ethyl acetate (20:1) gave about eight spots, R_f 0.33, 0.38, 0.45, 0.48, 0.51, 0.56, 0.72, and 0.90. Four of them were identical with those of benzoin (0.34), benzoin acetate (0.47), *trans*-DAS (0.51), and IAS (0.72). However, spots of *cis*-DAS (R_f 0.43) and benzil (R_f 0.67) could not be detected.

Reaction of DIS with Peracetic Acid in Propionic Acid.—Peracetic acid (1.5 mmol) in propionic acid (5 ml) containing 0.75 ml of acetic acid was added dropwise to the suspension of *trans*-DIS (1.2 mmol) in propionic acid (25 ml) at 70° over a period of 2 hr, and kept standing with stirring for 1 hr. After unreacted DIS was recovered by filtration (0.55 mmol, 46%), the filtrate was diluted with water and extracted with CCl_4. The extract was worked up as above, giving a yellow mixture, whose tlc in benzene showed three spots, R_f 0.63, 0.74, and 0.87. Two of them correspond to benzil (0.64) and tolan (0.87). A compound with R_f 0.74 was isolated by means of tlc in benzene, yielding 0.063 g of pale yellow solid, mp 77.5° (from *n*-hexane). The uv spectrum of this material was very similar to that of IAS. The ir spectrum (KBr), which was also similar to that of IAS, showed absorption bands at 1190, 1270, and 1750 cm^{-1} characteristic of

---

[20] Y. Ogata and I. Urasaki, *J. Chem. Soc. C*, 1689 (1970).

[21] H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 396 (1960).

[22] L. F. Fieser, "Experiments in Organic Chemistry," Maruzen, Tokyo, 1956, p 169.

[23] B. B. Corson and N. A. Saliani, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 69.

[24] R. Adams and V. Voorhees, *J. Amer. Chem. Soc.*, **41**, 789 (1919).

vinyl ester. The nmr spectrum (10% in CCl_4, standard TMS) showed signals at τ 2.34–3.00 (multiplet, C_6H_5), 8.00 (quartet, CH_2), and 9.16 (triplet, CH_3), their intensity ratio being 10:2:3. These data indicate that the compound is *trans*-α-iodo-α'-propionyloxystilbene (*trans*-IPS).

Anal. Calcd for $C_{17}H_{15}IO_2$: C, 53.98; H, 4.01; I, 33.55. Found: C, 53.7; H, 3.99; I, 33.7.

Rate Measurement for the Transfer of Active Oxygen from Peracetic Acid to Hexahydrobenzoic Acid.—Hexahydrobenzoic acid (9 ml) and 2 *M* peracetic acid in acetic acid (1 ml) were separately allowed to stand at 50° to reach temperature equilibrium, and then they were mixed quickly to start the reaction. Aliquots (each 1 ml) were pipetted out at known intervals of time and poured into a separatory funnel containing water (20 ml) and CCl_4 (5 ml). The funnel was shaken rapidly to extract hexahydrobenzoic and hexahydroperbenzoic acids. The extract was again washed with water (20 ml) and separated. The content of hexahydroperbenzoic acid in CCl_4 and that of peracetic acid in the combined aqueous layer were measured by iodometric titration with 0.02 *N* $Na_2S_2O_3$.

Registry No.—*trans*-IAS, 29478-23-7; *trans*-DAS, 35855-69-7; *trans*-DIS, 20432-11-5; *trans*-IPS, 36872-18-1; peracetic acid, 79-21-0; benzil, 134-81-6; sulfuric acid, 7664-93-9; sodium acetate, 127-09-3; iodine, 7553-56-2; anisole, 100-66-3; hexahydrobenzoic acid, 98-89-5.

CIDNP from Diffusive Encounters of Free Radicals. The Reaction of Trichloromethyl with Tetramethylethylene

HALVAR Y. LOKEN,[1] RONALD G. LAWLER,[2] AND HAROLD R. WARD*[2]

Metcalf Research Laboratories, Brown University, Providence, Rhode Island 02912

Received April 11, 1972

The trichloromethyl radical, formed by thermal decomposition of trichloroacetyl peroxide, reacts with tetramethylethylene predominantly by addition rather than by abstraction of an allylic hydrogen atom. The reaction between the adduct radical and another trichloromethyl radical proceeds primarily by donation of a hydrogen atom to form chloroform and 4,4,4-trichloro-2,3,3-trimethyl-1-butene. CIDNP emission signals with enhancement factors greater than 200 are observed for both products. At high tetramethylethylene concentration, radical pair substitution occurs.

The first observations[3] of chemically induced dynamic nuclear polarization (CIDNP) were tentatively explained[4,5] by an adaptation of the Overhauser effect. Free radicals were assumed to form with electron spin states equally populated and subsequent electron-nuclear cross relaxation was supposed to give rise to a nuclear polarization which could be retained in rapidly formed radical products. With this model it was difficult to explain polarization resulting from the diffusive encounter of free radicals, although a "reverse" Overhauser effect was suggested for this purpose.[6] It was at this point in the evolution of CIDNP that we began a study of the enhanced spectra taken during the thermolysis of trichloroacetyl peroxide, a system in which any proton polarization must necessarily result from the reactions of secondary radicals.[7] During the time that this study was underway, it was pointed out[6,8] that very large nuclear polarizations may be generated in the radicals reacting in and escaping from both geminate and diffusive encounter radical *pairs.* The results of our studies of the trichloroacetyl peroxide system are entirely in accord with the radical pair model, and, in addition, offer confirmation that proton polarization is not destroyed during hydrogen atom transfer from one radical to another. In the course of these studies, the reaction of tetramethylethylene (TME) with the trichloromethyl radical ($\cdot CCl_3$) has been examined in detail.

Results and Discussion

Reactions of $\cdot CCl_3$ with TME. Products.—TME was selected as a radical trap for $\cdot CCl_3$ because only one primary abstraction and one addition reaction are possible, and only a narrow region of the nmr spectrum (δ 1.5–1.7) is obscured by the allylic methyl absorption. The TME–$\cdot CCl_3$ reaction does not appear to have been investigated previously, and the ratio of addition to abstraction (X) is not known. Huyser[9] has, however, measured this ratio for *cis-* and *trans*-2-butene, for which it is found that $X = 34$ and 26, respectively, at 99° in the liquid phase. The additional methyl groups in TME should favor abstraction by a statistical factor of two, and also possibly enhance the polar character of the abstraction process, which has been suggested to involve a transition state with some electron transfer from the olefin to $\cdot CCl_3$.[10] Addition should also be accelerated by both the increased nucleophilicity of the double bond and the greater stability of the tertiary adduct radical, but decreased by steric crowding in the radical. The balancing of these effects is difficult to predict since one can find grounds on which to expect X to be both greater than and less than that for 2-butene.

Analyses of the products of the thermolysis of trichloroacetyl peroxide (0.08 *M*) in carbon tetrachloride were made as a function of TME concentration (Table I). Since the purpose of the product determinations was to support the CIDNP studies, reactions were run under the conditions used for recording CIDNP spectra; *e.g.*, an nmr tube containing the reagents at $< -10°$ was dropped into an nmr probe held at 60°. Under these conditions the reaction was complete in

---

[1] National Center for Air Pollution Control, Special Fellow (Predoctoral), 1967–1970.

[2] Alfred P. Sloan Foundation Research Fellow.

[3] J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch.*, **22a**, 1551 (1967); H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 5517 (1967); H. R. Ward and R. G. Lawler, *ibid.*, **89**, 5518 (1967).

[4] R. G. Lawler, *ibid.*, **89**, 5519 (1967).

[5] J. Bargon and H. Fischer, *Z. Naturforsch.*, **22a**, 1556 (1967).

[6] G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969).

[7] For another system where polarization must take place in a random encounter, see S. R. Fahrenholtz and A. M. Trozzolo, *ibid.*, **94**, 283 (1972).

[8] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195 (1969).

[9] E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

[10] E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 394 (1960).