phosphate (9.14 g, 0.035 mol) in ethyl ether (50 ml): yield of oil product 6.05 g (85%); ir C=O at 1760, P=O at 1283, P—O—C at 1020 cm^{-1}.

−**Preparation of Peroxy Acids. Peroxyanisic Acid.**—Hydrogen peroxide (3.4 g of 98% concentration, 0.10 mol) was added dropwise to a mixture of anisoyl diethyl phosphate (5.76 g, 0.02 mol) and methanesulfonic acid (0.96 g, 0.01 mol) in ethyl ether (10 ml) at 10–15°. After complete addition of hydrogen peroxide, the mixture was stirred for 90 min at room temperature. Ice-cold water was added (10 ml) and the peroxy acid was extracted with chloroform. The chloroform solution was water washed, briefly dried with anhydrous sodium sulfate, and evaporated to give peroxyanisic acid (3.36 g, 87% peroxy acid content by iodometric analysis.[1,16] The product was purified by recrystallization from chloroform (8 ml/g of peroxy acid) at 0°, mp 87–88° (lit.[17] 85–86°).

Other Peroxy Acids.—The peroxy acids were prepared by the procedure described for peroxyanisic acid using the following quantities of reactants. The reaction conditions, yields, and peroxy acid content are recorded in Table I.

3,4,5-Trimethoxyperoxybenzoic Acid.—Methanesulfonic acid (0.96 g, 0.01 mol) and H$_2$O$_2$ (1.7 g, 0.05 mol) were added to 3,4,5-trimethoxybenzoyl diethyl phosphate (3.48 g, 0.01 mol) dissolved in ethyl ether (10 ml) at 15°. The product (2.03 g, 88% peroxy acid content) was recrystallized from chloroform–petroleum ether (2:1, 15 ml) at −20°, mp 84–85°.

2,4,6-Trimethylperoxybenzoic Acid.—Methanesulfonic acid was not required as a catalyst for this preparation. H$_2$O$_2$ (3.4 g, 0.10 mol) was added to 2,4,6-trimethylbenzoyl diethyl phosphate (6.0 g, 0.02 mol) in ether (3 ml) at 0–5° and the reaction was completed at 15°. The product solidified from solution in 20 min (3.5 g, 80% peroxy acid content) and was recrystallized from ethyl ether–petroleum ether (5:3, 16 ml) at −20°, mp 55.5–57°. (Note that this compound is sometimes difficult to isolate in pure form. A semisolid peroxy acid was obtained from one preparation that spontaneously decomposed to tar with evolution of heat. In the case of studies not requiring the solid peroxy acid, it may be preferable to use the dried chloroform solution directly.)

p-Nitroperoxybenzoic Acid.—Methanesulfonic acid (0.67 g, 0.007 mol) and H$_2$O$_2$ (0.30 g, 0.075 mol) were added to a solution of p-nitrobenzoyl diethyl phosphate (1.0 g, 0.0035 mol) in ethyl ether (2 ml) at 25–30°. The product (0.85 g, 87% peroxy acid content) was recrystallized from chloroform (30 ml) at 0°, mp 138–139° (lit.[1] mp 138° dec).

(16) (a) D. H. Wheeler, *Oil Soap*, **9**, 89 (1932); (b) D. Swern, *Org. React.*, **7**, 392 (1953).

(17) C. G. Overberger and R. W. Cummins, *J. Amer. Chem. Soc.*, **75**, 4250 (1953).

o-Nitroperoxybenzoic Acid.—Methanesulfonic acid (1.96 g, 0.02 mol) and H$_2$O$_2$ (1.70 g, 0.05 mol) were added to a solution of o-nitrobenzoyl diethyl phosphate (3.03 g, 0.01 mol) in ethyl ether (5 ml) at 25–30°. The product (1.5 g, 74% peroxy acid content) was recrystallized from chloroform–petroleum ether (1:1, 40 ml/g) at 0°, mp 97–98° (lit.[1] mp 95–96°).

Peroxystearic Acid.—Methanesulfonic acid (0.98 g, 0.01 mol) and H$_2$O$_2$ (1.7 g, 0.05 mol) were added to a solution of stearoyl diethyl phosphate (4.21 g, 0.01 mol) in ethyl ether (15 ml) at 20° and the reaction was completed at 25–30°. The product (2.98 g, 92% peroxy acid content) was recrystallized from petroleum ether (20 ml/g) at 0°, mp 66–67° (lit.[1] mp 65°).

Peroxycinnamic Acid.—Methanesulfonic acid (0.96 g, 0.01 mol) and H$_2$O$_2$ (1.70 g, 0.05 mol) were added to a solution of cinnamoyl diethyl phosphate (2.94 g, 0.01 mol) in ethyl ether (3 ml). The product (1.60 g, 91% peroxy acid content) was recrystallized from chloroform–petroleum ether (1:2, 30 ml/g) at −20°, mp 75–76.5°.

Peroxypivalic Acid.—Methanesulfonic acid (1.96 g, 0.02 mol) and H$_2$O$_2$ (3.40 g, 0.10 mol) were added to a solution of pivaloyl diethyl phosphate (5.76 g, 0.02 mol) in ethyl ether (5 ml). A slight modification for the isolation of this low molecular weight peroxy acid was preferred to the use of chloroform as extraction solvent by the addition of ice and saturated ammonium sulfate solution and several extractions with olefin-free petroleum ether. The combined extracts were washed twice with ammonium sulfate solution, dried over anhydrous sodium sulfate, filtered, and analyzed volumetrically. The oily product (2.42 g, 98%) was recovered by evaporation of solvent but was not further purified.

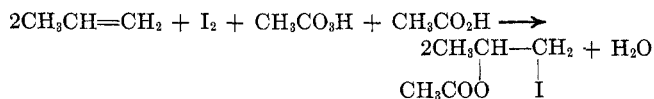# The Reaction of Tolan with a Mixture of Iodine and Peracetic Acid[1]

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

The reaction of tolan with a mixture of iodine and peracetic acid in acetic acid stereospecifically gave *trans*-α-iodo-α'-acetoxystilbene (IAS) together with benzil at 50° in the dark. IAS was oxidized by peracetic acid to form benzil much faster than tolan, implying that benzil obtained in the iodoacetoxylation of tolan is formed by way of IAS. The reaction at room temperature in dispersed light afforded *trans*-α,α'-diiodostilbene (DIS), which also gave IAS and benzil by the oxidation with peracetic acid. These results and some kinetic data suggest a mechanism involving slow formation of acetyl hypoiodite followed by its rapid addition to the triple bond.

In our previous papers[2,3] it has been reported that aliphatic olefins such as cyclohexene or propylene react easily with a mixture of iodine and peracetic acid in

$$2CH_3CH=CH_2 + I_2 + CH_3CO_3H + CH_3CO_2H \longrightarrow$$

$$2CH_3\underset{|}{CH}-\underset{|}{CH_2} + H_2O$$
$$CH_3COO \qquad I$$

acetic acid–ether at room temperature to give iodoacetoxy compounds, e.g., 1-iodo-2-acetoxypropane (ca. 80%) from propylene. The kinetic study suggests a mechanism involving a rate-determining attack of peracetic acid on the olefin–iodine π complex.

It is interesting to know how this mixture of iodine and peracetic acid reacts with acetylenic compounds. The reaction of acetylene with a mixture of iodine and peracetic acid was found to give diiododiacetoxyethane together with some other products, but no ole-

(1) Contribution No. 164.
(2) Y. Ogata, K. Aoki, and Y. Furuya, *Chem. Ind. (London)*, 304 (1965).
(3) Y. Ogata and K. Aoki, *J. Org. Chem.*, **31**, 1625 (1966).

Table I

Reaction of Tolan with a Mixture of Iodine and Peracetic Acid in Acetic Acid to Form
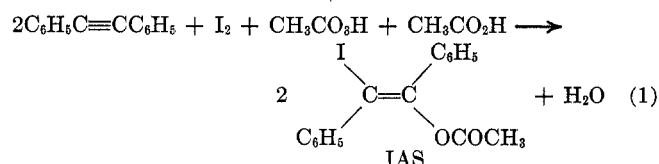α-Iodo-α'-acetoxystilbene (IAS) and Benzil[a]

| ————Initial concn of reactants, M———— | | | Catalyst, N | | ————Yield, %[b]———— | |
[PhC≡CPh]	[I₂]	[AcO₂H]	(H₂SO₄)	Temp, °C	IAS	Benzil
0.10	0.055	0.055	0	50	63	17
0.10	0.055	0.055	0	50	74	14[c]
0.060	0.033	0.033	0	50	56	16[d]
0.10	0.055	0.055	0	70	57	15
0.067	0.067	0.067	0	50	57	43
0.10	0.055	0.055	0.05	50	38	36
0.10	0.055	0.055	0.20	50	23	39
0.10	0	0.11	0	50	0	6

[a] Reaction time, 10 hr at 50° and 5 hr at 70°. [b] Yield based on original tolan was estimated by means of uv spectrophotometry.
[c] Acetic acid solutions of tolan and peracetic acid were simultaneously added dropwise to an acetic acid solution of iodine with stirring.
In the other runs the reactants were all mixed in acetic acid at the beginning of the reaction. [d] Reaction in 90% aqueous acetic acid.

finic compounds were obtained.[4] On the other hand, the addition of chlorine, hydrochloric acid, bromine, or N-bromosuccinimide (NBS) to phenyl- or diphenylacetylenes in acetic acid gave the corresponding cis and trans olefins in fairly good yields.[5–11] For example, the reaction of diphenylacetylenes with NBS in aqueous acetic acid gave α-bromo-α'-acetoxystilbene together with α,α-dibromodeoxybenzoin, and the mechanism involving a rate-determining electrophilic attack of hypobromous acid on the triple bond was postulated.[8,12] The present paper describes our results on the reaction of tolan with iodine–peracetic acid in acetic acid, which was found to give iodoacetoxystilbene and benzil. The mechanism of the reaction will be discussed on the basis of the results.

Results and Discussion

The reaction of tolan with a mixture of iodine and peracetic acid in acetic acid at 50° in the dark gave trans-α-iodo-α'-acetoxystilbene (abbreviated to IAS) in ca. 70% yield (eq 1). This product was identified

$$2C_6H_5C{\equiv}CC_6H_5 + I_2 + CH_3CO_3H + CH_3CO_2H \longrightarrow$$

$$2 \quad \underset{C_6H_5}{\overset{I}{\diagdown}} C{=}C \underset{OCOCH_3}{\overset{C_6H_5}{\diagup}} + H_2O \quad (1)$$

IAS

by infrared and nmr spectra and elementary analysis. The configuration was assigned on the basis of nmr spectra, i.e., τ 8.24 (singlet) for the methyl group of trans-IAS, because the signal is quite similar to that at τ 8.17 (singlet) of trans-α-bromo-α'-acetoxystilbene, rather than 7.79 of its cis isomer, both of which were obtained by the reaction of tolan with NBS in aqueous acetic acid.[8] The deshielding of iodine in cis-iodoacetoxystilbene as observed in cis-bromoacetoxystilbene would also operate to the similar extent. Therefore, the obtained iodoacetoxystilbene having the mp 146° is surely the trans isomer. Fur-

(4) Y. Ogata, K. Aoki, and Y. Shibata, The 19th Annual Meeting of Chemical Society of Japan at Yokohama, 1966.

(5) H. Sinn, S. Hopperdietzel, and D. Sauermann, Monatsh. Chem., 96, 1036 (1965).

(6) Yu. A. Serguchev and E. A. Shilov, Ukr. Khim. Zh., 32, 34 (1966); Chem. Abstr., 65, 585c (1966).

(7) R. C. Fahey and D. J. Lee, J. Amer. Chem. Soc., 88, 5555 (1966).

(8) A. Jovtscheff and S. L. Spassov, Monatsh. Chem., 98, 2272 (1967).

(9) R. C. Fahey and D. J. Lee, J. Amer. Chem. Soc., 90, 2124 (1968).

(10) J. A. Pincock and K. Yates, ibid., 90, 5643 (1968).

(11) J. König and V. Wolf, Tetrahedron Lett., 1629 (1970).

(12) A. Jovtscheff and S. L. Spassov, Monatsh. Chem., 100, 328 (1969).

ther, no cis isomer was formed in the iodoacetoxylation of tolan, since the methyl nmr spectra of the reaction mixture gave only a signal at τ 8.24.

When equimolar amounts of reactants were used, a considerable yield of benzil (ca. 40%) was obtained together with IAS, as shown in Table I. Although oxidation of tolan with peracids also gives benzil,[13,14] the yield was low compared with that in the iodoacetoxylation of tolan (eq 2, Table I). This fact

$$C_6H_5C{\equiv}CC_6H_5 + 2RCO_3H \longrightarrow C_6H_5COCOC_6H_5 + 2RCO_2H$$
$$(2)$$
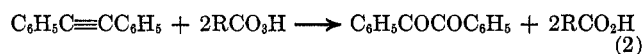
suggests that benzil produced in iodoacetoxylation is formed not from a direct oxidation of tolan with peracetic acid but from a successive oxidation of some intermediate with peracetic acid. In fact, the peracetic acid oxidation of IAS gave benzil in a good yield, liberating a molecular iodine, as shown in Table II and eq 3. Hence, most of the benzil produced is
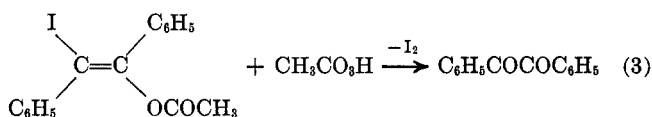
$$\underset{C_6H_5}{\overset{I}{\diagdown}} C{=}C \underset{OCOCH_3}{\overset{C_6H_5}{\diagup}} + CH_3CO_3H \xrightarrow{-I_2} C_6H_5COCOC_6H_5 \quad (3)$$

Table II

Reaction of α-Iodo-α'-acetoxystilbene (IAS) with Peracetic Acid in Acetic Acid to Form Benzil

| Initial amount ——of reactants—— | | Volume of | ——Reaction—— | | |
IAS, mmol	AcO₂H, mmol	solvent, AcOH, ml	Temp, °C	Time, hr	Yield,[a] %
1.0	1.1	20	50	10	49
2.0	2.2	25	70	5	64[b]

[a] Yield was estimated by means of uv spectrophotometry.
[b] Peracetic acid in acetic acid was slowly added with stirring to IAS in acetic acid.

probably the result of the successive oxidation of IAS with peracetic acid; the amount of benzil produced from the direct oxidation of tolan with peracetic acid may be neglected. This is confirmed also by the kinetic data (Table III).

As shown in Table I, the yield of IAS and/or benzil is not so affected by the addition of water to the reaction system. This behavior is different from the result in iodoacetoxylation of olefins, where the addition of water considerably lowers the yield.[3] The reaction at higher temperature gave rather low yield

(13) R. N. McDonald and P. A. Schwab, J. Amer. Chem. Soc., 86, 4866 (1964).

(14) J. K. Stille and D. D. Whitehurst, ibid., 86, 4871 (1964).

of IAS and/or benzil, probably because the decomposition of peracetic acid became faster. With increasing molar ratio of the reagent, the yield of benzil rises, but the yield of IAS falls down, probably because IAS is further oxidized with excess peracetic acid. Moreover, the addition of sulfuric acid lowers the yield of IAS and raises the yield of benzil. This indicates that the oxidation of IAS with peracetic acid is catalyzed by sulfuric acid, while iodoacetoxylation is not an acid catalysis.

It is known that benzil is oxidized with peracetic acid to give benzoic acid.[15] However, the oxidation is slow, the value of the second-order rate constant being *ca.* 10^{-4} M^{-1} sec^{-1} at 70°, which is about a hundred times as small as that for the oxidation of IAS with peracetic acid to form benzil. Hence, the formation of benzoic acid in the iodoacetoxylation of tolan with iodine–peracetic acid can be neglected. Virtually no benzoic acid was detected in the present reaction.

As obvious in Table III, the rate of the reaction of IAS with peracetic acid is about a hundred times
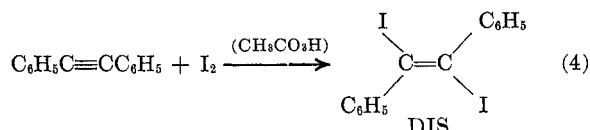
TABLE III

SECOND-ORDER INITIAL RATE CONSTANTS FOR THE
REACTION OF PERACETIC ACID IN ACETIC ACID AT 50°

Substrate[a]	——Initial concn, M——.		$k_2{}^b \times 10^3$,
	[I₂]	[AcO₂H]	M^{-1} sec^{-1}
Tolan	0	0.05	0.03
IAS	0	0.05	2.8
Tolan	0.05	0.05	1.3 (0.6,[c] 1.2[d])
	0.05	0.05	1.2 (1.3[c])

[a] Initial concentration of the substrate was 0.05 *M.* [b] Rate constant for the consumption of peracetic acid. [c] Rate constant for the consumption of iodine. [d] Rate constant for the consumption of tolan measured by means of uv spectrophotometry.

as fast as that of the peracetic acid oxidation of tolan. The rate of the consumption of peracetic acid and/or iodine in the reaction of tolan with a mixture of iodine and peracetic acid is almost the same as that in the reaction of iodine and peracetic acid alone (Table III). Such a phenomenon has been observed in the iodination of aromatic compound with a mixture of iodine and peracetic acid.[16] In contrast, iodoacetoxylation of olefin is fast, the second-order rate constant k_2 being *ca.* 5 × 10^{-2} M^{-1} sec^{-1} at 30° which is *ca.* 300-fold of that in the reaction of iodine with peracetic acid.[3] Hence, the mechanism proposed for the iodination of aromatic compound with iodine–peracetic acid, where the reaction of iodine with peracetic acid forming acyl hypohalite is rate determining, may be applied for the iodoacetoxylation of tolan.

It was found that *trans*-α,α'-diiodostilbene (DIS) was produced in 2 weeks in *ca.* 80% yield based on original iodine, when the reaction of tolan with iodine–peracetic acid was carried out at room temperature in 50 vol % acetic acid–ether under dispersed light (eq 4). Under these conditions the rate of consumption

$$C_6H_5C{\equiv}CC_6H_5 + I_2 \xrightarrow{(CH_3CO_3H)} \underset{C_6H_5}{\overset{I}{\diagdown}}C{=}C\underset{I}{\overset{C_6H_5}{\diagup}} \quad (4)$$
DIS

(15) Y. Furuya and I. Urasaki, *Bull. Chem. Soc. Jap.,* **41**, 660 (1968).
(16) Y. Ogata and K. Nakajima, *Tetrahedron,* **20**, 43 (1964).

of iodine was slow, but after 1 day colorless crystals of DIS began to precipitate. The precipitate was identified by ir spectrum, mixture melting point determination, and elementary analysis.

Here, the formation of DIS in the reaction of tolan with iodine alone (6% yield in 6 days) was slower than that in the presence of peracetic acid (80% yield in 2 weeks). Further, the formation of DIS in the reaction of tolan with a mixture of iodine and peracetic acid also was slower in the dark (11% yield in 18 days). These results suggest that the formation of DIS proceeds mainly in a radical mechanism. Peracetic acid and/or a small amount of acetyl peroxide present in peracetic acid may affect the radical reaction.

Since the activation energy of a radical addition reaction is generally small (2–3 kcal/mol),[17] it is expected that the ionic reaction (iodoacetoxylation) is preferred to the radical addition at higher temperature. In fact, DIS was not virtually formed in the dark at 50°, which supports ionic character of the iodoacetoxylation and radical nature of the formation of DIS. An evidence for the radical nature is the acceleration of the reaction of tolan with iodine to form DIS by irradiation of light (39% yield in 3.5 hr) and/or by addition of benzoyl peroxide (18% yield in 5 hr at 70°).

DIS also reacted with peracetic acid yielding IAS (37%), benzil (30%), and liberating iodine (eq 5, Table IV). However, IAS is not formed *via* DIS in the iodo-
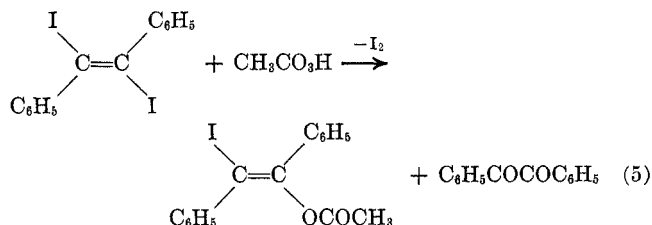
$$\underset{C_6H_5}{\overset{I}{\diagdown}}C{=}C\underset{I}{\overset{C_6H_5}{\diagup}} + CH_3CO_3H \xrightarrow{-I_2}$$

$$\underset{C_6H_5}{\overset{I}{\diagdown}}C{=}C\underset{OCOCH_3}{\overset{C_6H_5}{\diagup}} + C_6H_5COCOC_6H_5 \quad (5)$$

TABLE IV

REACTION OF α,α'-DIIODOSTILBENE (DIS) WITH
PERACETIC ACID IN ACETIC ACID TO FORM
α-IODO-α'-ACETOXYSTILBENE (IAS) AND BENZIL[a]

Initial amount of reactants——.		Volume of	——Reaction——.		——Yield[b]——.	
DIS, mmol	AcO₂H, mmol	solvent, AcOH, ml	Temp, °C	Time, hr	IAS, %	Benzil, %
2.0	2.0	20	50	10	20	22
2.0	2.2	25	70	5	37	30[c]

[a] Suspended solution of DIS was always stirred. [b] Yield based on original DIS was estimated by means of uv spectrophotometry. [c] Peracetic acid in acetic acid was slowly added with stirring to the suspension of DIS in acetic acid.

acetoxylation of tolan, since no DIS was obtained in the reaction of tolan with iodine alone in acetic acid at 50° in the dark.

The cis addition of chlorine or hydrochloric acid to tolan or phenylpropyne is more favorable than trans addition,[6,7,9] but the trans adduct is favored in the reaction of tolan or phenylpropyne with bromine or NBS in aqueous acetic acid.[8,10] The present iodoacetoxylation is specific trans addition, which suggests that the configuration of the transition state in these additions depends on the size of halogen atoms; thus, a

(17) M. Takahashi, "Chemistry of Free Radicals," H. Sakurai and K. Tokumaru, Ed., Nankodo, Tokyo, Japan, 1967, p 30.

larger halogen gives a lower cis:trans ratio of the adducts.

As described above, the reaction of acetylene itself with a mixture of iodine and peracetic acid gave no olefin, but saturated compounds.[4] This is explained by a higher reactivity of olefins than the corresponding acetylenes in the electrophilic addition reaction, whereas tolan gave olefinic products (IAS). This fact may be due to the resonance stabilization of the product, where the double bond is conjugated with the benzene rings. Hence, most of the other additions to phenyl- or diphenylacetylenes give also olefinic products.[5-11,18] Furthermore, the steric interaction between large iodine atoms and/or between an iodine atom and a benzene ring may inhibit the addition to iodo olefins. In spite of the easy addition of bromine to stilbene,[19] the addition of iodine or acyl hypoiodite to stilbene was found to be difficult.

Two kinds of mechanisms have been postulated for the addition reaction of acetylenes: one is a mechanism involving a nucleophilic addition of bromide ion to the triple bond as proposed for bromine addition to acetylenes,[5,20] and the other is an electrophilic addition proposed for the bromoacetoxylation of diphenyl-acetylenes with NBS in 80-90% aqueous acetic acid.[12] In the latter, acetyl hypobromite (CH$_3$CO$_2$Br), formed by the reaction of NBS with water and then with acetic acid, may attack the triple bond forming an ion pair via a π complex, because acetyl hypobromite is more electrophilic than hypobromous acid (eq 6).


(6)
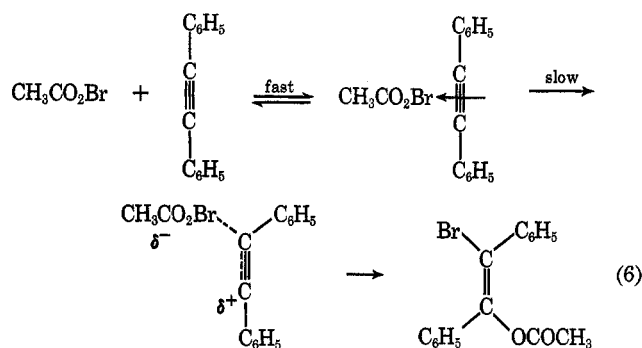
The present iodoacetoxylation is quite similar to bromoacetoxylation except for a higher trans:cis ratio of the products. The iodoacetoxylation of tolan is an electrophilic addition, since its rate is low compared with that of iodoacetoxylation of olefins.

In view of these facts, the following two mechanisms are conceivable (eq 7-9): (a) a rate-determining attack of peracetic acid on the tolan–iodine π complex which has been proposed by us for the iodoacetoxylation of olefins,[3] and (b) the slow formation of acetyl hypoiodite followed by its rapid addition to tolan, as postulated for aromatic iodination.[16] Step 9 cannot be slower than step 8, because the rate of the consumption of tolan in the present reaction is the same as that of the formation of acetyl hypoiodite (Table III). Though these two cannot be distinguished by the present data, mechanism b seems to be more probable than mechanism a, because the rate of consumption of peracetic acid or iodine in the reaction of iodine

Mechanism a

(7)

Mechanism b

$$I_2 + CH_3CO_3H + CH_3CO_2H \xrightarrow{slow} 2CH_3CO_2I + H_2O \quad (8)$$

(9)
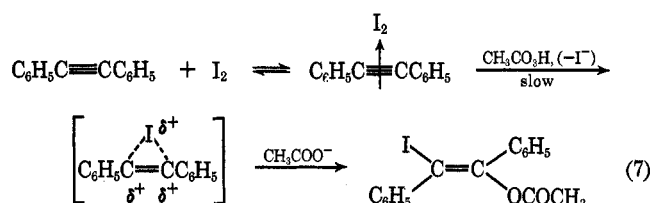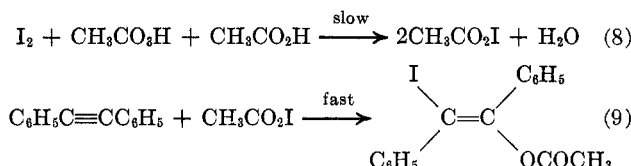
with peracetic acid alone (*i.e.*, the formation of acetyl hypoiodite or hypoiodous acid) is not affected by addition of tolan to this reaction system, and in this sense iodoacetoxylation of tolan is similar to the bromo-acetoxylation reaction with NBS.

The formation of acetyl hypoiodite in the reaction of iodine with peracetic acid has not been proved directly. In the thermal decomposition of phenyl iodine diacetate, acetyl hypoiodite has been postulated as an intermediate which decomposes to give methyl iodide and carbon dioxide, though acetyl hypoiodite has never been isolated.[21] Hence, if acetyl hypoiodite is formed in a mixture of acetic acid, peracetic acid, and iodine, then the formation of methyl iodide and carbon dioxide via decarboxylation of acetyl hypoiodite may be observed under appropriate reaction conditions when the unsaturated substrate is absent (eq 10). The

$$CH_3CO_2I \longrightarrow CH_3I + CO_2 \quad (10)$$

isolation of methyl iodide in this reaction was expected to be difficult, because it is easily oxidized with per-acetic acid to methyl acetate (eq 11).[22] Nevertheless,

$$CH_3I + CH_3CO_3H \longrightarrow CH_3CO_2CH_3 + HOI \quad (11)$$

both methyl iodide and methyl acetate could eventually be detected by means of glpc from the mixture of acetic acid, peracetic acid, and iodine, as described in the Experimental Section. Carbon dioxide was also produced in 12.3% yield at 70°. Only 0.6% yield of carbon dioxide was produced from peracetic acid in acetic acid alone under the same conditions. These results may be a satisfactory evidence for the formation of acetyl hypoiodite.

Experimental Section

Materials.—About 3.5 *M* peracetic acid was prepared by the reaction of acetic anhydride with 60% H$_2$O$_2$ in the presence of a catalytic amount of H$_2$SO$_4$.[23] Stilbene was prepared by the reduction of benzoin with zinc amalgam,[24] mp 124-125° (from 95% ethanol) (lit. mp 124°). Tolan was prepared from stilbene by the debromination of stilbene dibromide with KOH in EtOH,[25] mp 60.5-61° (from 95% ethanol)(lit. mp 60-61°). Commercial 99.5% acetic acid was purified by rectification (bp 117-119°). Iodine was purified by the sublimation.

(18) T. J. Barton and R. G. Zika, *J. Org. Chem.*, **35**, 1729 (1970).
(19) G. Heublein and E. Mlejnek, *Z. Chem.*, **7**, 340 (1967).
(20) H. Sinn, *Z. Elektrochem.*, **61**, 989 (1957).

(21) J. E. Leffler and L. J. Story, *J. Amer. Chem. Soc.*, **89**, 2333 (1967).
(22) Y. Ogata and K. Aoki, *J. Org. Chem.*, **34**, 3974 (1969).
(23) Y. Ogata and I. Urasaki, *J. Chem. Soc. C*, 1689 (1970).
(24) R. L. Shriner and A. Berger, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 786.
(25) L. I. Smith and M. M. Falkof, ref 24, p 350.

Iodoacetoxylation of Tolan. *trans-α-Iodo-α'-acetoxystilbene* **(IAS).**—Tolan, iodine, and peracetic acid (each 5 mmol) were dissolved in acetic acid (50 ml) in the dark and then kept standing at 50° for 10 hr. At the end of the reaction *ca.* 33% of iodine was consumed. The reaction mixture was diluted with water, being extracted with ether or chloroform. The extract was washed successively with aqueous KI, aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and then with water. The dried (Na_2SO_4) organic layer was removed from the solvent under reduced pressure, yielding residual pale yellow solid (1.31 g) which gave yellow crystals of IAS (0.68 g) by the fractional crystallization from methanol. Additional IAS (0.136 g) was isolated from the filtrate by means of column chromatography on silica gel using benzene as eluent, so that the total yield of isolated IAS was 0.817 g (44.9% based on original tolan), mp 146–146.5° (from methanol).

A methanol solution of this material showed only an inflection at about 250 mμ (ϵ 11,000), being similar to the spectra of α-substituted or α,α'-disubstituted stilbenes.[26] The ir spectrum (KBr) showed absorption bands at 1194, 1220, and 1760 (CO—OC=C), 1370 (CH_3), and 1500 and 3000–3070 cm^{-1} (C_6H_5). Nmr spectrum (20% in $CDCl_3$, standard TMS) showed signals at τ 2.3–3.0 (multiplet, C_6H_5) and 8.24 (singlet, $CH_3COO—$), and their intensity ratio was 10:3. These data indicate the presence of an acetoxyl group at the α position of stilbene.

Anal. Calcd for $C_{16}H_{13}IO_2$: C, 52.77; H, 3.60; I, 34.85. Found: C, 52.79; H, 3.33; I, 34.8.

Identification of Benzil.—The residue (0.575 g) recovered from the above filtrate of IAS was chromatographed on silica gel in benzene, yielding 0.136 g of IAS (R_f 0.74 in tlc) and 0.321 g (30.6% yield) of benzil (R_f 0.69), which on recrystallization from methanol gave mp and mmp 95°.

Addition of Iodine to Tolan. *trans-α,α'-Diiodostilbene* **(DIS).**—Tolan (10 mmol), iodine (5 mmol), and peracetic acid (5 mmol) were dissolved in 50 vol % acetic acid–ether (50 ml) and kept at room temperature in the dispersed light. In a few days precipitate began to occur. After 2 weeks the precipitate was filtered off, washed with methanol, and dried, yielding 1.80 g of DIS (84% yield based on iodine); recrystallization from $CHCl_3$ gave mp and mmp (in a sealed tube) 191° dec (lit.[26] mp 199° dec).

A methanol solution of this material showed almost the same uv spectrum as tolan, indicating the decomposition of DIS to tolan and iodine in methanol. It has been reported that DIS is slightly decomposed also in *n*-hexane.[26] The ir spectrum (KBr) showed absorption bands at 550 (CI) and 1700–2000 and 3000–3080 cm^{-1} (C_6H_5). The nmr spectrum could not be obtained because of the poor solubility of DIS.

Anal. Calcd for $C_{14}H_{10}I_2$: C, 38.92; H, 2.33; I, 58.75. Found: C, 38.68; H, 2.39; I, 59.0.

An authentic sample of DIS was obtained by the reaction of tolan with iodine in acetic acid at room temperature. After 6 days the yield of precipitated DIS was only 6% of the theoretical amount. Recrystallization from $CHCl_3$ gave mp of 191° dec in a sealed tube.

Reaction of Tolan with Peracetic Acid.—An acetic acid solution (20 ml) of tolan (2 mmol) and peracetic acid (2.2 mmol) was kept standing at 50° for 10 hr. The reaction mixture was diluted with water and extracted with chloroform. The extract was washed with aqueous $NaHCO_3$ and water and then dried (Na_2SO_4). Evaporation of solvent *in vacuo* gave a solid which

(26) H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 396 (1960).

consisted of unreacted tolan (94%) and benzil (6%), according to the tlc-analysis and uv spectrophotometry.

Reaction of IAS with Peracetic Acid.—Peracetic acid (2.2 mmol) was added slowly to IAS (2 mmol) in acetic acid at 70° over a period of 5 hr. The reaction mixture which contained iodine liberated was diluted with water and extracted with chloroform. The extract, worked up as above, gave yellow solid containing IAS and benzil by means of tlc analysis, the yield of benzil being 64% according to the uv spectrophotometry.

Reaction of DIS with Peracetic Acid.—The suspension of DIS (2 mmol) in acetic acid (20 ml) was added with peracetic acid (2.2 mmol) in acetic acid (5 ml) at 70° over a period of 5 hr, iodine being liberated as the reaction proceeded. After unreacted DIS being recovered by filtration (0.284 g, 32.9%), the filtrate was diluted with water and extracted with chloroform. The extract was worked up as above to yield yellow solid containing IAS (37%) and benzil (30%) (tlc and uv spectrophotometry).

Ultraviolet Spectrophotometry.—A methanolic solutions of three components (tolan, IAS, and benzil) of known concentrations were prepared and extinctions at 230, 258 and 296 mμ were measured by a Hitachi double beam uv–visible spectrophotometer, Model 124. The compositions calculated from the extinctions and molecular absorption coefficient of each component agreed with the theoretical within 1% error. Since the main products were IAS and benzil, the estimation was done assuming the reaction mixture consisted of only the three components.

Typical Procedure for the Rate Measurements.—Separate acetic acid solutions of 0.105 *M* tolan, 0.1 *M* iodine, and 2.0 *M* peracetic acid were allowed to stand at 50° to reach temperature equilibrium. Aliquots (9.5 ml, 10 ml, and 0.5 ml, respectively) were pipetted out from the solutions and they were mixed quickly to start the reaction, giving each 0.1 *M* reactant solution. Aliquots (each 2 ml) were pipetted out at known intervals of time and placed in a separatory funnel containing distilled water (40 ml) and CCl_4 (20 ml). The content of iodine in CCl_4 and that of peracetic acid in aqueous layer were measured iodometrically. Sometimes, the titrated CCl_4 layer was then analyzed by means of uv spectrophotometry.

Detection of Carbon Dioxide, Methyl Iodide, and Methyl Acetate in the Reaction of Iodine with Peracetic Acid.—An acetic acid solution (33 ml) of *ca.* 3 *M* peracetic acid (0.1 mol) was added dropwise with stirring to an acetic acid solution (50 ml) of iodine (0.01 mol) in a three-necked flask fitted with a reflux condenser at *ca.* 70° during 30 min. Then, nitrogen gas was slowly bubbled into the reaction mixture for *ca.* 30 min. The gaseous and volatilized products passing through the reflux condenser were trapped with Dry Ice–methanol, and carbon dioxide was then taken up with a saturated aqueous $Ba(OH)_2$, the precipitated $BaCO_3$ being filtered off and dried. Trapped products were identified by means of glpc employing a Yanagimoto Model GCG 550 F with a flame ionization detector operated with a 1.5 m × 3 mm column packed with Apiezon L grease 15% on Celite 545 of 80–100 mesh using N_2 as a carrier (20 ml/min) at 40° and H_2 in a flow rate of 20 ml/min. Retention times were 2.1 and 3.2 min for methyl acetate and methyl iodide, respectively.