Anal. Calcd for $C_{11}H_{16}$ (2,5-dihydro-5-phenyl-*cis*-2-pentene): C, 89.19; H, 10.81. Found: C, 89.39; H, 10.79.

Reduction of 2,5-Dihydroallylbenzene. Undivided Cell, Ethanol Present.—Lithium chloride (5 g, 0.12 mol), absolute ethanol (4 g, 0.09 mol), and 2 g of material (87% 2,5-dihydroallylbenzene and 13% 2,5-dihydro-*n*-propylbenzene)[27] were placed in a 100-cc three-neck flask along with 60 cc of methylamine. A current of 0.5 A was passed through the system for 1 hr and 46 min (3180 C). The product, 1.8 g (90%), was shown by glpc (4-ft, LAC 446 column, 60°) to consist of 2,5-dihydroallylbenzene (34%) and 2,5-dihydro-*n*-propylbenzene (66%) as adjudged by their respective retention times.

Anal. Calcd for C_9H_{12} (2,5-dihydroallylbenzene): C, 89.94; H, 10.06. Found: C, 89.96; H, 10.09.

Reduction of 2,5-Dihydro-4-phenyl-1-butene. Undivided Cell, Ethanol Present.—Lithium chloride (5 g, 0.12 mol), absolute ethanol (4 g, 0.09 mol), and 1.5 g of material (90% 2,5-dihydro-4-phenyl-1-butene, 5% 2,5-dihydro-*n*-butylbenzene, and 5% 4-phenyl-1-butene)[28] were electrolyzed in a 100-cc three-neck flask by passing a current (0.5 A) for 76 min (2280 C). There was obtained 1.2 g (80%) of material consisting of 2,5-dihydro-*n*-butylbenzene (31%) and 2,5-dihydro-4-phenyl-1-butene (69%). These compounds were identified by matching their retention times (glpc) with the products obtained from the reductions of 4-phenyl-1-butene (Table VI).

Reduction of 2,5-Dihydro-5-phenyl-1-pentene. Undivided Cell, Ethanol Present.—In a manner completely analogous to that described above for the dihydro-1-butene, 1.3 g of material[29] [2,5-dihydro-5-phenyl-1-pentene (95%) and 5-phenyl-1-pentene (5%)] was electrolyzed by passing a current (0.5 A) for 59 min (1770 C). The product (1.2 g, 91%) consisted of (analysis by glpc, 20-ft, 25% Carbowax 1540 column, 150°) 5-phenyl-1-pentene (3%), 2,5-dihydro-5-phenyl-1-pentene, (76%), and 2,5-dihydro-*n*-pentylbenzene (21%).

Anal. Calcd for $C_{11}H_{16}$ (2,5-dihydro-5-phenyl-1-pentene): C, 89.19; H, 10.81. Found: C, 89.15; H, 10.95.

Registry No.—(2,5-Dihydro-5-phenyl)-*cis*-2-pentene, 21893-20-9; 2,5-dihydroallylbenzene, 21902-31-8; (2,5-dihydro-5-phenyl)-1-pentene, 21902-32-9; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *cis*-4-octene, 7642-15-1; allylbenzene, 300-57-2; 4-phenyl-1-butene, 768-56-9.

Acknowledgment.—This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force under AFOSR Grant 822-67.

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[27] This material was obtained by preparative glpc (a combination of a 15-ft, 24% Zonyl E-7 column and a 15-ft 24% Carbowax 20 M column was used) from the products of the reactions described in Table V.

[28] A mixture obtained by preparative glpc (same columns and conditions as described in ref 27) from the products of the reactions summarized in Table VI.

[29] Obtained by preparative glpc (same columns and conditions as described in ref 27) from the products of reduction of 5-phenyl-1-pentene.

Reaction of Alkyl Iodides with Peracetic Acid in the Presence of Aromatic Compounds[1]

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Treatment of *n*-alkyl iodides with peracetic acid in the presence of aromatic compounds in acetic acid at 30° affords alkyl acetates and often iodo aromatic compounds in good yields. The rate of the reaction for a mixture of methyl iodide, peracetic acid, and *m*-xylene can be expressed as $v = k[CH_3I][CH_3CO_3H]$ and is independent of the concentration of *m*-xylene. The structure of alkyl iodides affects the yield of iodoaromatic compound in the decreasing order *n*-alkyl > *sec*-alkyl > *t*-alkyl. The reaction mechanism is briefly discussed in terms of the effect of structure on the kinetics and product composition.

Among the reactions of alkyl iodides, the substitution of iodide by nucleophilic reagents such as hydroxide, phenoxide, alkoxide, and halide ions and other solvent molecules has been studied extensively.[2] The kinetic studies on oxidation with peracids which have electrophilic oxygen have been reported, *e.g.*, epoxidation of olefins and oxidation of aldehydes, ketones, amines, aromatic hydrocarbons, and sulfur compounds.[3,4] Also, oxidation of iodide ion by peracids or by peroxides has been used as a standard method for the quantitative analysis of peroxides or peracids.[5,6] During our kinetic study of iodoacetoxylation of olefins, it was observed that alkyl iodides liberate iodine on treatment with peracetic acid.[7] However, few reports have thus far appeared on the oxidation of alkyl iodides with peracids.[8]

There are several methods for iodination of aromatic compounds with molecular iodine, and these reactions usually require oxidizing agents such as nitric acid, periodic acid, sulfur trioxide, peroxides, or silver sulfate.[9,10] We have previously suggested an aromatic iodination with a mixture of iodine and peracetic acid and postulated a mechanism explaining its autocatalytic nature.[9]

We have found that molecular iodine in the above reaction can be replaced by alkyl iodide in some cases, and we wish to report in the present paper a novel aromatic iodination with a mixture of alkyl iodides and peracetic acid in acetic acid, which is exemplified by

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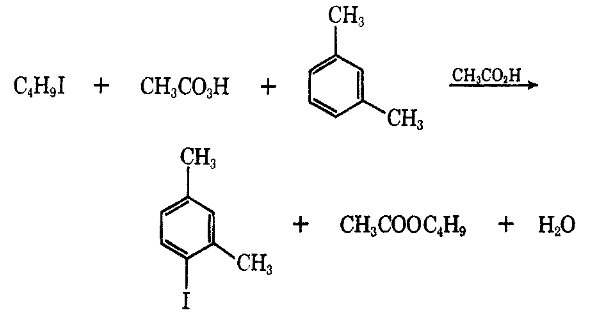
TABLE I

REACTION OF ALKYL IODIDES (RI) AND PERACETIC ACID IN THE PRESENCE OF *m*-XYLENE (ArH) IN ACETIC ACID AT 30°

Alkyl group, R	Reactants, × 10² *M* RI	CH_3CO_3H	ArH	Reaction time, days	Products, × 10² *M*[a,b] RI[c]	CH_3CO_2R (%)	ArI[d] (%)	I_2 (%)
Methyl	9.89	3.60	8.17	180[e]	Some	Some	2.64 (73)	0.02 (1)
Ethyl	5.04	2.03	8.06	2	Some	Some	1.51 (74)	0.03 (3)
n-Propyl	4.92	2.39	8.08	10	2.55	1.66 (70)	1.59 (66)	0.04 (4)
Isopropyl	4.92	2.27	8.07	9	0.80	2.79 (123)	0.02 (0.8)	1.69 (149)
n-Butyl	4.93	2.29	8.06	9	2.57	1.78 (78)	1.81 (79)	0.01 (1)
Isobutyl	2.54	1.41	8.12	14	1.13	Small	1.00 (71)	0.02 (3)
sec-Butyl	2.57	1.36	8.10	6	0.82	0.61 (45)	0.01 (0.6)	0.30 (44)
t-Butyl	2.43	1.36	8.12	6	Small	0.93 (69)	0.00 (0)	0.93 (137)
n-Amyl	2.56	1.47	8.08	16	1.20	1.06 (72)	1.13 (77)	0.02 (3)
Isoamyl	4.99	2.04	8.05	2	2.92	1.13 (55)	0.57 (28)	0.47 (46)
n-Hexyl	2.53	1.46	8.11	16	1.31	1.06 (73)	1.08 (74)	0.03 (4)
n-Octyl	4.64	2.03	8.05	2	2.32	1.55 (76)	1.01 (51)	0.15 (20)
Cyclohexyl	4.89	2.03	8.05	3	Some	Small	0.00 (0)	0.21 (20)
Benzyl	2.44	1.40	8.09	12	Small	1.98 (141)	0.19 (13)[f]	1.00 (143)

[a] Yields are based on peracetic acid used. [b] Some or small means that quantitative analysis has not been done. [c] Recovered. [d] Iodo-*m*-xylene. [e] Minutes. [f] Bibenzyl was not detected in the products.

the reaction of *n*-butyl iodide with a mixture of peracetic acid and *m*-xylene (eq 1).



(1)

Results and Discussion

The reaction of a mixture of alkyl iodide, peracetic acid, and an aromatic compound was carried out in acetic acid at 30°. The results are shown in Table I. The table shows that the stoichiometry of the reaction can be expressed as in eq 2. Isobutyl iodide gives a high yield of aromatic iodide but a low yield of isobutyl acetate. Isoamyl iodide affords a lower yield of iodo aromatics than other primary iodides.

$$RI + CH_3CO_3H + ArH \xrightarrow{\text{in } CH_3CO_2H} ArI + CH_3COOR + H_2O \quad (2)$$

R = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, and *n*-hexyl;
ArH = *m*-xylene or mesitylene

Secondary alkyl iodides such as isopropyl and *sec*-butyl iodides give very poor yields of aromatic iodide, where a large amount of molecular iodine is liberated. No iodo-*m*-xylene was obtained with cyclohexyl iodide. With benzyl iodide, benzyl acetate and iodine are the main products and a low yield of iodo-*m*-xylene is obtained. No bibenzyl, *i.e.*, a coupling product of benzyl radical, is detected by glpc. In the reaction of *t*-butyl iodide, *t*-butyl acetate and iodine, but no iodo-*m*-xylene, were obtained.

The reaction of alkyl iodide with peracetic acid without aromatic compound under the same conditions affords high yields of iodine and alkyl acetates as confirmed by glpc analysis.

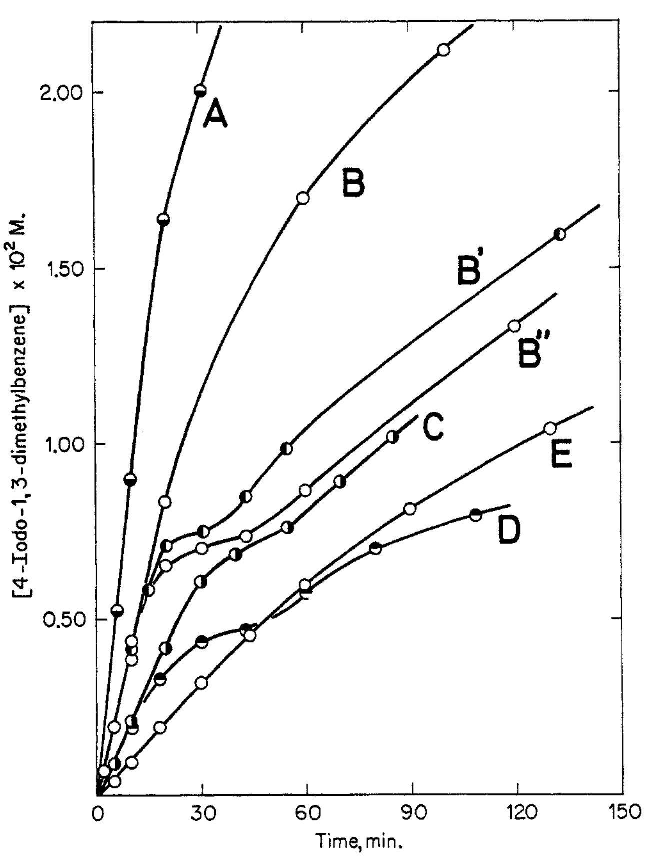


Figure 1.—Reaction of methyl iodide, peracetic acid, and *m*-xylene in acetic acid at 30°. Conversion curves of formation of iodo-*m*-xylene. Initial concentrations are the same as those in Table II.

Kinetic study was conducted in acetic acid at 30° by estimating the rate of formation of iodo aromatic compound and the rate of consumption of peracetic acid. As seen in Figures 1 and 2, Tables II and III, the rate of the reaction of methyl iodide–peracetic acid–*m*-xylene at an early stage can be expressed as $v = k[CH_3I][CH_3CO_3H]$, and it is independent of the concentration of *m*-xylene. The value of the calculated rate constant decreased with the progress of the reaction, probably because of the liberation of iodine, which is less reactive than alkyl iodide. The rate is first-order both in methyl iodide and peracetic acid. The average rate constant *k* for the formation of iodo-*m*-xylene is $2.09 \times 10^{-3}\ M^{-1}\ sec^{-1}$ and it is nearly equal

TABLE II

SECOND-ORDER RATE CONSTANTS OF THE REACTION OF METHYL IODIDE–PERACETIC ACID–*m*-XYLENE IN ACETIC ACID AT 30° AND THE YIELD OF IODO AROMATIC COMPOUND

Concentration × 10² *M*			Time, min	Concentration × 10² *M*, ArI (%)[a]	Curve in Figure 1	k^b × 10³ M^{-1} sec^{-1}
CH_3I	CH_3CO_3H	*m*-Xylene				
9.95	7.20	8.15	300	4.51 (63)	A	2.23
10.00	3.50	10.03	1500	2.08 (60)	. . .	2.35
9.89	3.60	8.17	180	2.64 (73)	B	2.15
9.94	1.80	8.24	500	1.04 (58)	D	1.84
4.98	3.60	8.23	490	2.11 (59)	C	2.14
2.54	3.60	8.18	2330	2.12 (84)	E	2.21
9.93	3.60	4.11	350	1.90 (53)	B′	2.01
9.96	3.60	2.11	2320	1.95 (93)	B″	1.85
10.01	3.60	10.14[c]	484	2.45 (68)[d]		1.97
10.04	2.00[e]	10.09	366	0.01 (0.6)		
						Av 2.09

[a] The yield of iodo-*m*-xylene is based on the reactant of the smallest amount. [b] Rate constant k was calculated from iodo-*m*-xylene formation by $v = k[CH_3I][CH_3CO_3H]$ at an early stage of the reaction. [c] Mesitylene. [d] Iodomesitylene. The yield was 79% after 16 days. [e] Phenyl iodine diacetate.

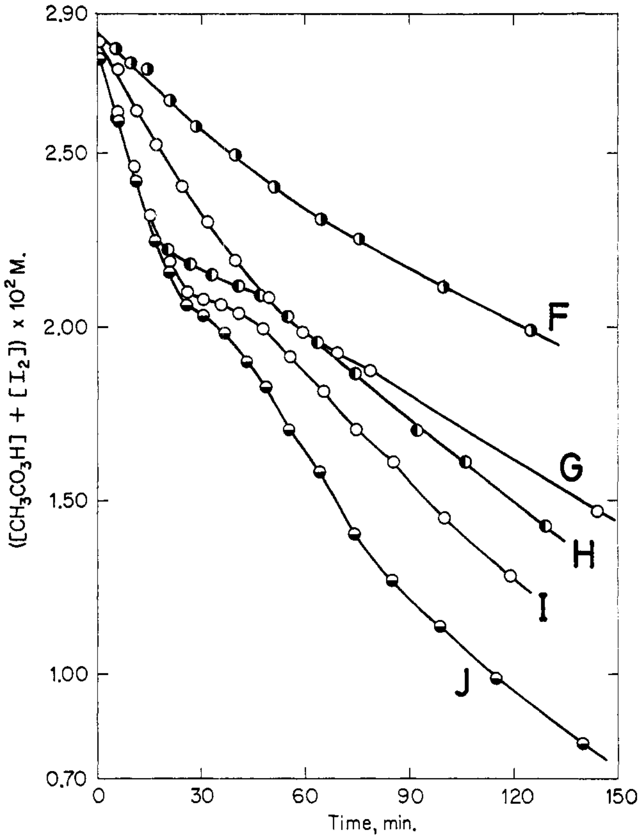


Figure 2.—Reaction of methyl iodide, peracetic acid, and *m*-xylene in acetic acid at 30°. Conversion curves of consumption of peracetic acid. Initial concentrations are the same as those in Table III.

to that for the consumption of peracetic acid (2.21 × 10^{-3} M^{-1} sec^{-1}). The rate of formation of iodomesitylene is the same as that of iodo-*m*-xylene, showing that the rate-determining step is the bimolecular reaction of alkyl iodide and peracetic acid.

The effect of alkyl group of alkyl iodide on the rate constant $k \times 10^3$ M^{-1} sec^{-1} for iodination of *m*-xylene calculated from peracetic acid consumption is as follows: CH_3, 2.2; C_2H_5, 4.0; *n*-C_4H_9, 5.0. This observed reactivity of alkyl iodides toward peracetic acid, $CH_3I < C_2H_5I <$ *n*-C_4H_9I, is reverse to that of the ordinary S_N2-type reaction,[2] and it suggests that the present reaction is of electrophilic or of S_E2 type in nature.

TABLE III

SECOND-ORDER RATE CONSTANTS OF THE REACTION OF METHYL IODIDE–PERACETIC ACID–*m*-XYLENE IN ACETIC ACID AT 30°

Concentration × 10² *M*			Curve in Figure 2	k^a × 10³ M^{-1} sec^{-1}
CH_3I	CH_3CO_3H	*m*-Xylene		
10.27	5.80	8.10		2.28
10.27	5.83	8.10		2.27
10.20	2.93	8.09		2.09
10.33	2.90	8.12		2.12
5.11	5.76	8.11		2.38
5.14	2.84	8.14	G	2.24
2.52	2.85	8.14	F	2.35
10.19	2.79	16.21	J	2.07
10.24	2.85	4.02	I	2.22
10.43	2.81	1.96	H	2.10
				Av 2.21

[a] Rate constant k was calculated from peracetic acid consumption by $v = k[CH_3I][CH_3CO_3H]$ at an early stage of the reaction.

The reaction of *n*-alkyl iodide is generally accompanied by the liberation of a small amount of iodine; this occurs to a remarkable extent with *n*-propyl, *n*-hexyl, and *n*-octyl iodides, but only to a small extent with ethyl iodide and especially with *n*-butyl, *n*-amyl, and methyl iodides. The amount of formed iodine increases at early stages of the reaction when molar ratios $[CH_3I]/[CH_3CO_3H]$ and $[CH_3I]/[$*m*-xylene$]$ increase in the reaction of methyl iodide–peracetic acid–*m*-xylene, in view of the coloration of iodine and also curves H, I, and J in Figure 2. The yields of iodine and iodo-*m*-xylene change with the structure of alkyl iodides, as shown in Table I. These facts indicate the competition between aromatic iodination and liberation of iodine (eq 5 and 6). It was confirmed that *n*-alkyl and *sec*-alkyl iodides are stable toward solvolysis in an acetic acid solution under these conditions.

We have reported that an iodo aromatic compound is oxidized by peracetic acid to aryl iodine diacetate, which is a more active oxidant than peracetic acid in the aromatic iodination with iodine.[9] When peracetic acid was replaced by phenyl iodine diacetate in acetic acid at 30° in a reaction with methyl iodide–*m*-xylene, the yield of iodo-*m*-xylene became very low, as shown in the last line of Table II. This result suggests that alkyl iodide is very slowly oxidized by aryl iodine diacetate, which is an effective oxidizing agent for the acceleration of aromatic iodination.[9] Therefore, no autocatalysis is observed in the present reaction and the possible formation of aryl iodine diacetate may have an effect to lower the yield of iodo-*m*-xylene in the present reaction.

Unlike aryl iodide, alkyl iodide cannot afford stable alkyl iodine diacetate.[8] Hence, the reaction of alkyl iodides with peracetic acid in acetic acid in the absence of aromatic compound affords molecular iodine and alkyl acetates in good yield, whereas in the presence of an aromatic compound, iodination of the aromatic compound occurs.

The mechanism of the aromatic iodination at initial stages of the reaction may be expressed as shown in eq 3–5, which fit the fact that the rate is independent of the concentration of the aromatic compound, ArH.

$$\mathrm{RI + CH_3CO_3H \xrightarrow{slow} HOI + CH_3OOR} \qquad (3)$$

$$\mathrm{HOI + CH_3CO_2H \overset{fast}{\rightleftharpoons} CH_3CO_2I + H_2O} \qquad (4)$$

$$\mathrm{ArH + CH_3CO_2I \xrightarrow{fast} ArI + CH_3CO_2H} \qquad (5)$$

Liberation of iodine may arise from reaction 6.

$$\mathrm{RI + CH_3CO_2I \xrightarrow{fast} CH_3CO_2R + I_2} \qquad (6)$$

From the kinetic results it can be seen that aromatic iodination does not take place with molecular iodine *via* eq 6 and 7, but through active iodinating agents

$$\mathrm{I_2 + CH_3CO_3H + 2ArH \longrightarrow 2ArI + H_2O + CH_3CO_2H} \qquad (7)$$

such as CH_3CO_2I or HOI which is formed by the bimolecular reaction of alkyl iodide with peracetic acid. Thus, the rate of the reaction of iodine with peracetic acid in acetic acid is expressed as $v = k[I_2][CH_3CO_3H]$, where k is *ca.* $2 \times 10^{-4}\ M^{-1}\ \mathrm{sec}^{-1}$ at 30°,[7] which is a much lower rate than that for the reaction of alkyl iodide and peracetic acid in the presence and absence of aromatic compounds.

Equation 3 might proceed either by direct electrophilic bimolecular substitution reaction or *via* an unstable aliphatic iodoso compound or iodoso diacetate.

In the case of *n*-alkyl iodides, the reaction proceeds mainly by eq 3, 4, and 5, while in the case of *sec*- and *t*-alkyl iodides the reaction may go by way of eq 3, 4 and 6.

Equation 6 is preferred to eq 5 in secondary and tertiary alkyl iodides, probably because the abstraction of iodide ion from RI by iodonium ion derived from CH_3COOI is easier than from the corresponding primary iodide.

Experimental Section

Materials.—Commercial methyl and ethyl iodides of reagent grade were used without further purification. Other alkyl iodides were prepared by refluxing respective alcohols with a mixture of iodine and red phosphorus.[11] Benzyl iodide was prepared by refluxing benzyl chloride and potassium iodide in ethanol.[12] Boiling points of the prepared iodides are indicated as follows: *n*-propyl, bp 101.7–102.3°; isopropyl, bp 88.7–89.0°; *n*-butyl, bp 130–131°; isobutyl, bp 119–120.5°; *sec*-butyl, bp 119.0–120.0°; *t*-butyl, bp 28° (47 mm); *n*-amyl, bp 77.0–77.2° (65 mm); isoamyl, bp 145–147°; *n*-hexyl, bp 83–85° (36 mm); *n*-octyl, bp 65.5–72.0° (2 mm); cyclohexyl, bp 59.0–59.8° (7 mm); benzyl, bp 79–80° (5 mm).

Commercial methyl, ethyl, and *n*-butyl acetates of reagent grade were used for the authentic samples of glpc analysis without further purification. Other alkyl acetates were prepared by sulfuric acid catalyzed esterification of the corresponding alcohols with acetic acid in general[13] or with acetic anhydride and zinc dust in cases of *n*-octyl and *t*-butyl acetates.[14] Boiling points of prepared alkyl acetates are indicated as follows: *n*-propyl, bp 101–102°; isopropyl, bp 87–88°; *n*-butyl, bp 125–126°; isobutyl, bp 115–117.3°; *sec*-butyl, bp 110–112.5°; *t*-butyl, bp 95–97.5°; *n*-amyl, bp 60–61° (31 mm); isoamyl, bp 141–142°; *n*-hexyl, bp 78.1–80.2° (31 mm); *n*-octyl, bp 118–123° (44 mm); cyclohexyl, bp 173–175°; benzyl, bp 110° (30 mm).

Acetic acid for the kinetic solvent was purified by rectifying 99.5% acetic acid over P_2O_5, bp 117.5–118.0°. An acetic acid solution of peracetic acid was prepared by the method described previously.[15] Authentic samples, iodotoluene, bp 204–207°, 4-iodo-1,3-dimethylbenzene, bp 126–129° (28 mm), and iodomesitylene, mp 31°, were prepared by the reaction of toluene, *m*-xylene, or mesitylene with a mixture of iodine and peracetic acid.[9,16]

Analyses of Reaction Products.—The products were analyzed by glpc employing a Yanagimoto Model GCG 550F with a flame ionization detector operated with a 2 m × 3 mm column packed with Apiezon L grease 15% on Celite 545 of 80–100 mesh using nitrogen as a carrier (10–20 ml/min) at 30–200°, hydrogen flow rate 20–30 ml/min, injection temperature 240–330°, and detector temperature 240–330°. Identification of products was also done by means of glpc using PEG 20M (3%) 2 m × 3 mm and Silicone SE 30 2 m × 3 mm columns. A 2 m × 3 mm column of Apiezon L grease 15% was the most convenient of the three columns. Retention times were longer in the order of alcohols, alkyl acetates, alkyl iodides, and iodo-*m*-xylene for the samples used in this investigation. Benzene, toluene, or chlorobenzene were used as solvents to extract products from the reaction mixture. Iodotoluene was used as an internal standard for the estimation of iodo-*m*-xylene by glpc at 160°, and alkyl iodides or alkyl acetates were used as internal standards for the estimation of other products at a lower column temperature of 30–120°. All internal standards were added to the extract of the reaction products just before the analyses by glpc. The results are indicated in Table I. Infrared spectra were determined by a Perkin-Elmer Model 333 spectrophotometer.

Rate Measurements.—The rate of the reaction of an alkyl iodide, peracetic acid, and *m*-xylene in acetic acid at 30.0 ± 0.1° was followed generally as described previously.[9] Aliquots of the reaction mixture were pipetted out into an ice-cooled aqueous potassium iodide solution at known intervals of time and the amount of peracetic acid was titrated by 0.01 *N* $Na_2S_2O_3$. In some runs, the concentration of formed iodo-*m*-xylene was measured by glpc. Second-order rate constants were calculated at an early stage of the reaction in most cases because a complex reaction may often occur at a later stage of the reaction. The results are indicated in Figures 1 and 2 and Tables II and III.

Registry No.—Peracetic acid, 79-21-0; *m*-xylene, 108-38-3; iodomethane, 74-88-4; iodoethane, 75-03-6; 1-iodopropane, 107-08-4; 2-iodopropane, 75-30-9; 1-iodobutane, 542-69-8; 1-iodo-2-methylpropane, 513-38-2; 2-iodobutane, 513-48-4; 2-iodo-2-methylpropane, 558-17-8; 1-iodopentane, 628-17-1; 1-iodo-3-methylbutane, 541-28-6; 1-iodohexane, 638-45-9; 1-iodooctane 629-27-6; iodocyclohexane, 626-62-0; α-iodotoluene, 620-05-3.

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