Table XIV
Retention Times

| Compd | Min |
|---|---|
| Adamantane | 9.5 |
| 1-Methyladamantane | 10.2 |
| 1,3-Dimethyladamantane | 10.7 |
| 1,3,5-Trimethyladamantane | 11.0 |
| 1,3,5,7-Tetramethyladamantane (VI) | 11.2 |
| 1-Ethyladamantane | 16.8 |
| 1-Ethyl-3-methyladamantane | 16.8 |
| 1,3-Dimethyl-5-ethyladamantane (V) | 17.6 |
| Perhydrophenalene (*trans*) | 25.4 |
| Perhydrophenalene (*cis*) | 29.2 |
| 2-Methylperhydrophenalene (*e*) (IV) | 31.2 |
| 1-Methylperhydrophenalene (*e*) | 33.4 |
| 2-Methylperhydrophenalene (*a*) | 36.0 |
| *trans,syn,trans*-Perhydroanthracene (I) | 40.3 |
| *trans,anti,trans*-Perhydrophenanthrene (II) | 41.6 |
| *cis,syn,trans*-Perhydroanthracene (III) | 45.0 |
| Perhydroanthracene-1 (I) | 40.3 |
| Perhydroanthracene-2 | 46.0 |
| Perhydroanthracene-3 | 52.6 |
| Perhydroanthracene-4 | 55.0 |
| Perhydrophenanthrene-1 | 45.2 |
| Perhydrophenanthrene-2 | 51.8 |
| Perhydrophenanthrene-3 | 58.8 |
| Perhydrofluorene-1 | 26.1 |
| Perhydrofluorene-2 | 30.1 |
| Perhydrofluorene-3 | 32.5 |
| Perhydroacenaphthene-1 | 18.2 |
| Perhydroacenaphthene-2 | 19.7 |
| Perhydroacenaphthene-3 | 22.5 |
| Perhydroacenaphthene-4 | 25.0 |

of the experiments leading to formation of the perhydrophenalenes and the initial isomerization products of the perhydrophenanthrenes is warranted.

**Perhydrophenalenes.**—A bright yellow-orange aluminum bromide complex prepared from 5 g of aluminum bromide, 8 ml of mixed dimethylhexanes, and hydrogen bromide at 50° was decanted from excess paraffin and washed at 0° with 5 ml of methylcyclohexane. Still at 0°, the decanted complex was shaken for 3 min with perhydrofluorene (10 ml, *ca.* 8.5 g) and a slight warming of the mixture was noticed. The supernatant organic phase was quickly decanted from the complex (which showed no signs of change), washed with 10% aqueous potassium hydroxide, and dried over sodium sulfate. The product, recovered in essentially quantitative yield, displayed one large and one very small peak in vpc. Trapping of the large peak in the product gave the previously described[1] product melting at around 0° and this was characterized by dehydrogenation to phenalene, mp 58.0–64.5° (lit. mp 68–69°), and by nmr.

***trans,syn,trans*-Perhydroanthracene** (I).—Complex prepared from 10 g of aluminum bromide, 16 ml of dimethylhexanes, and hydrogen bromide at 50° was shaken at 0° with 3.0 ml of the liquid mixture of perhydrophenanthrenes. In less than 1 min the organic phase crystallized completely and a sample taken at this point showed one large peak in vpc amounting to 90% of the product and having a retention time identical with that of the lowest boiling isomer of the mixture obtained in the hydrogenation of anthracene. This retention time is appreciably shorter than any of the isomers in the mixture of perhydrophenanthrenes. The washed sample was solid and recrystallization from hot ethanol gave colorless needles, mp 86.2–88.0° (lit. mp 90°). The complex was unchanged in volume, color, and viscosity.

**Methylperhydrophenalenes.**—The above-mentioned experiment was continued at 0° by adding an additional 37.0 ml of the perhydrophenanthrenes (total of 37.6 g) and 4.1 g of aluminum bromide and saturating with hydrogen bromide. In less than 2 min of shaking, complete solidification occurred again. Shaking was continued while the mixture was warmed to room temperature in a water bath and within 12 min complete melting to a nonviscous liquid had occurred. After a total reaction time of 40 min at 27°, the product, no longer crystallizable on cooling to 0°, was separated from the complex which had undergone no visible change. Very little perhydroanthracene could be found in this product by glpc. After washing with aqueous potassium hydroxide and drying, the product was distilled at 14 mm through a 10-in. Vigreux column. The following fractions were collected: 1, bp 90–120°, 3.8 g; 2, bp 120–125°, 4.7 g; 3, bp 125–128°, 22.4 g, $n^{20}_{D}$ 1.4927, mp 12.5–16°; 4, bp 128°, 1.5 g; residue, 0.6. Fraction 3 was crystallized and filtered at −5° giving 6.2 g of fine white needles. Crystallization from methyl ethyl ketone gave a solid, mp 31.5–32.5°. This material corresponds to the lowest boiling of the methylperhydrophenalene peaks in vpc.

**Equilibration of Perhydrophenanthrene in a Solvent.**—In order to observe the initial isomerization of the perhydrophenanthrenes without the disturbing effect on equilibrium of crystallization of one of the components, a solution of perhydrophenanthrenes (5.0 ml, 4.70 g) in methylcyclohexane (10 ml) was shaken for 37 min at 0° with complex made from 5.0 g of aluminum bromide, 8.0 ml of dimethylhexanes, and hydrogen bromide. The hydrocarbon phase was decanted, washed with 10% aqueous potassium hydroxide, and dried over sodium sulfate; the solvent was removed under vacuum leaving a partly crystalline residue (3.82 g). The analysis of the product at this point by glpc is given in Table I. Recrystallization from hot, absolute ethanol gave I, mp 86.2–88.0°.

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# Haloacyloxylation. I. The Reaction of Propylene with a Mixture of Iodine and Peracetic Acid[1]

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The reaction of propylene with a mixture of iodine and peracetic acid in a mixed solvent of acetic acid and ethyl ether at 15–40° has been found to give 1-iodo-2-acetoxypropane in 54–80% yield. The kinetic study in acetic acid at 30° suggests a mechanism involving a rate-determining attack of peracetic acid on an olefin–iodine $\pi$ complex.

In our kinetic study on the iodination or bromination of aromatic compounds by a mixture of halogen and peracetic acid, it has been postulated that acyl hypohalite ($CH_3COOI$ or $CH_3COOBr$) is a probable attacking species.[2-4]

The reaction of olefin with a mixture of silver carboxylate and molecular halogen to form haloester (Prévost reaction)[5] probably goes by way of the same acyl hypohalite.

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[1] Contribution No. 83.

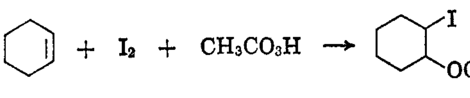
[2] Y. Ogata and K. Nakajima, *Tetrahedron*, **20**, 43 (1964).

[3] Y. Ogata and K. Nakajima, *ibid.*, **20**, 2751 (1964).

[4] Y. Ogata, Y. Furuya, and K. Okano, *Bull. Chem. Soc. Japan*, **37**, 960 (1964).

[5] (a) M. C. Prévost, *Compt. Rend.*, **196**, 1129 (1933); (b) M. C. Prévost, *ibid.*, **197**, 1661 (1933); (c) J. Kleinberg, *Chem. Rev.* **40**, 381 (1947); (d) R. G. Johnson and R. K. Ingham, *ibid.*, **56**, 219 (1956); (e) C. V. Wilson, *Org. Reactions*, **9**, 350 (1957); (f) M. I. Uschakov and W. O. Tchistov, *Ber.*, **68**, 824 (1935); (g) K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 6256 (1957); (h) F. D. Gunstone and L. J. Morris, *J. Chem. Soc.*, 487 (1957).

Therefore, it is of interest to study the reaction of olefin with a mixture of halogen and percarboxylic acid. In our preliminary paper,[6] we reported that the reaction of cyclohexene with a mixture of iodine and peracetic acid gives 1-iodo-2-acetoxycyclohexane (14.5–27.3%) together with 1,2-diacetoxycyclohexane.



This type of reaction is applicable to other olefins such as propylene. As described below, the kinetic study showed that the mechanism of reaction is not simple as in the aromatic iodination, since the addition of iodine to olefin is faster than the reaction of iodine and peracetic acid. For the kinetic study, propylene was chosen because of the simple and readily isolable products formed. The rates of conceivable elementary reactions were measured.

## Experimental Section

**Materials.**—Peracetic acid was prepared by the introduction of 30% hydrogen peroxide (200 ml) to a mixture of acetic anhydride (920 ml) and concentrated sulfuric acid (11 ml) at 30–40°.[7] The obtained 1.5–1.3 *M* peracetic acid solution contained small amounts of hydrogen peroxide and diacetyl peroxide; the solution could be stored for a few weeks without appreciable decomposition in a refrigerator; no stabilizer is needed for the storage. Propylene of 99.5% purity was purchased from Sinclair Refinery Co. Acetic acid for kinetic use was 99.5% pure. Commercial ethyl ether was used without further purification.

**Iodoacetoxylation of Propylene. 1-Iodo-2-acetoxypropane.**—An acetic acid solution (200 ml) of *ca.* 1.35 *M* peracetic acid was introduced dropwise to a stirred ethereal solution (200 ml) of iodine (38 g, 0.15 mole) at 16–19° over a period of 3.5 hr and propylene (3.9 moles) was bubbled simultaneously through the solution over a period of 6.5 hr. The reaction mixture became colorless and transparent at the end of reaction. After standing for *ca.* 20 hr, the mixture was diluted with water and then extracted with ether. The extract was washed successively with aqueous sodium bicarbonate, aqueous sodium hydroxide, and then with aqueous sodium thiosulfate. The dried organic layer was removed from the solvent under reduced pressure at *ca.* 20°, yielding a residual liquid (56.0 g, iodine content 54.61%) having an ester-like odor (80.4% yield based on original iodine). The vacuum distillation of the liquid gave 1-iodo-2-acetoxypropane,[8] bp 33.5–35.5° (0.7–0.8 mm), which was easily decomposed on ordinary distillation but could be stored in a desiccator in a refrigerator for several weeks: $d^{20}$ 1.67, $n^{20}{}_{D}$ 1.500.

*Anal.* Calcd for $C_5H_9IO_2$: C, 26.33; H, 3.98; I, 55.66; sapon. value, 492. Found: C, 25.94; H, 4.16; I, 55.30; sapon. value, 484.

A methanol solution of this material shows an absorption maximum at 358 m$\mu$. The infrared spectrum (liquid film) shows strong absorption at 1740 and 1240 cm$^{-1}$ characteristic of acetoxyl groups. Other bands were at 2970 (m), 2920 (w), 1450 (m), 1410 (m), 1370 (s), 1315 (m), 1180 (m), 1135 (m), 1125 (m), 1070 (m), 1047 (s), 1023 (s), 950 (m), and 600 cm$^{-1}$ (m). Nmr spectrum ($CCl_4$ solution, standard TMS) shows signals at $\tau$ 8.64 (doublet), 7.93 (singlet), 6.67 (doublet), and 5.17 (multiplet) and their intensity ratio is 3:3:2:1. These data indicate the presence of an acetoxyl group at the 2-position of propane.[9]

**The Addition of Iodine to Propylene. 1,2-Diiodopropane.**—Propylene (0.5 mole) was passed through a 50 vol % ether–acetic acid solution (400 ml) of iodine (38 g, 0.15 mole) at 17–21° over a period of 7.5 hr. About 85% of iodine was consumed. After *ca.* 20 hr, the reaction mixture was extracted with ether and the extract was washed with aqueous sodium hydroxide and then with aqueous sodium thiosulfate. The organic layer, after drying over anhydrous sodium sulfate, was pumped free of solvent at 15°. The residual liquid (24.9 g) was 1,2-diiodopropane (55% yield based on original iodine) with *ca.* 98% purity plus a small amount of 1-iodo-2-acetoxypropane: $d^{20}$ 2.4 (lit.[10] $d^{18.5}$ 2.490), $n^{20}{}_{D}$ 1.644. The product was easily decomposed on distillation or on storage over an extended period of time.

Infrared spectrum shows peaks at 2970 (m), 2910 (m), 1450 (s), 1425 (m), 1375 (s), 1290 (w), 1202 (w), 1185 (s), 1125 (vs), 1108 (vs), 1018 (s), 985 (m), 805 (w), and 490 cm$^{-1}$ (vs). The product has a peak characteristic for 1,2-dihalide (490 cm$^{-1}$), but no appreciable peaks for acetoxyl group (1740 and 1240 cm$^{-1}$).

*Anal.* Calcd for $C_3H_6I_2$: I, 85.78. Found: I, 84.13.

**The Reaction of 1,2-Diiodopropane with Peracetic Acid.**—Propylene (2.0 moles) was passed into an ethereal solution (400 ml) of iodine (38 g) at 15–23° over a period of 6 hr. About 70% of iodine was consumed. Without isolating 1,2-diiodopropane, an acetic acid solution (100 ml) of 1.5 *M* peracetic acid was added dropwise to the solution at 18–31° over a period of 4 hr. The mixture, after *ca.* 20 hr, was extracted with ether, and worked up as above, giving 1-iodo-2-acetoxypropane, 7.5 g (11% based on iodine), together with a small amount of recovered 1,2-diiodopropane. The identification of the product was accomplished by means of infrared spectra.

**The Effect of Addition of Sulfuric Acid on the Reaction of Propylene and Iodine.**—Propylene (2.2 moles) was passed into a 50 vol % acetic acid–ether solution (400 ml) containing concentrated sulfuric acid (2 ml) and iodine (38 g) at 24–32° for a period of 13.5 hr. After 3 days, the mixture was worked up as above to give 1-iodo-2-acetoxypropane, 7.4 g (11% based on iodine), containing a small amount of 1,2-diiodopropane. The product was identified by infrared spectrum.

**The Reaction of Propylene and Peracetic Acid. 1,2-Diacetoxypropane.**—Propylene (3.9 moles) was passed into a 50 vol % ether–acetic acid solution (400 ml) of peracetic acid (0.27 mole) at 18–19° over a period of 10 hr. After standing 112 days, the product was extracted with ether and worked up as above, giving 1,2-diacetoxypropane, 10.4 g (24% based on peracetic acid), bp 51–52° (1.3 mm), $d^{20}$ 1.05, $n^{20}{}_{D}$ 1.4139 (lit.[11] $d^{20}$ 1.0547, $n^{20}{}_{D}$ 1.4121). The infrared spectrum shows very strong absorptions at 1740 and 1240 cm$^{-1}$ for the acetoxyl group. Other peaks were at 2975 (m), 1430 (m), 1370 (s), 1160 (m), 1118 (m), 1080 (s), 1047 (s), 1016 (s), 955 (m), 900 (w), 840 (w), 820 (w), and 603 cm$^{-1}$ (m).

**The Prévost Type Reaction Using Mercuric Acetate,[5e,12] Iodine, and Propylene.**—To ether (200 ml) containing a suspension of mercuric acetate (16 g, 0.05 mole) was added dropwise an ethereal solution (200 ml) of iodine (25.4 g, 0.1 mole) over a period of 45 min at 21–26°, and propylene (0.7 mole) was passed into the solution simultaneously over a period of 1.2 hr. After standing 3 days, the precipitated mercuric iodide was removed by filtration. The filtrate was worked up as above, giving 1-iodo-2-acetoxypropane, 10.9 g (24% based on iodine), containing a small amount of 1,2-diiodopropane. The product was identified by infrared spectrum.

**A Typical Procedure for the Rate Measurements.**—An acetic acid solution of propylene was prepared by passing propylene through acetic acid at 30°, the concentration of propylene being *ca.* 0.296 *M* (estimated by Wijs's method[13]). The solution (73 ml), an acetic acid solution (25 ml) of 0.1 *M* iodine, and an acetic acid solution (2 ml) of 1.3 *M* peracetic acid in three separate flasks were allowed to stand at 30° to reach temperature equilibrium and were then mixed quickly to start the reaction. Aliquots (each 5 ml) were pipetted out at known intervals of time and placed in a separatory funnel containing distilled water (50 ml) and carbon tetrachloride (25 ml). The content of iodine in carbon tetrachloride and the content of peracetic acid in the aqueous layer were measured iodometrically by sodium thiosulfate. The blank test showed that this method for the analysis

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(7) D. Swern, *Org. Reactions*, **7**, 395 (1953).

(8) S. Z. Ivin, *Zh. Obshch. Khim.*, **28**, 180 (1958); *Chem. Abstr.*, **52**, 12829 (1958).

(9) The chemical shifts were calculated for isomers from the tables in L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Ltd., London, 1959.

(10) Beilstein's "Handbuch der Organischen Chemie," Hw. **1**, p 115.

(11) R. E. Dunbar and L. L. Bolstad, *J. Org. Chem.*, **21**, 1041 (1956).

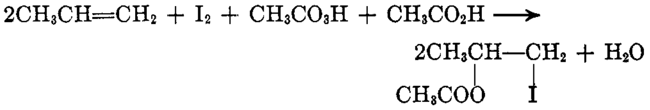
(12) L. Brunel, *Bull. Soc. Chim. France*, **33**, 382 (1905).

(13) An acetic acid solution (5 ml) of propylene was added to a mixture of acetic acid solution (25 ml) of 0.1 *M* iodine chloride and carbon tetrachloride (10 ml). After *ca.* 1 hr, a solution of *ca.* 10% potassium iodide (20 ml) and then water (100 ml) was added to the solution and the liberated iodine was titrated with aqueous sodium thiosulfate.

of iodine and peracetic acid gave satisfactory estimates within ±3% error.[2]

## Results and Discussion

It is apparent on the basis of nmr and infrared spectra and elementary analysis that the reaction of propylene with a mixture of iodine and peracetic acid produces 1-iodo-2-acetoxypropane in *ca.* 80% yield (iodoacetoxylation reaction). The addition of water lowers the yield (Table I).



$$2CH_3CH{=}CH_2 + I_2 + CH_3CO_3H + CH_3CO_2H \longrightarrow 2\underset{\displaystyle CH_3COO}{CH_3CH}{-}\underset{\displaystyle I}{CH_2} + H_2O$$

The product was identical with the Prévost type reaction product obtained from mercuric acetate, iodine, and propylene. Analogous reaction is observed with other olefins, *e.g.*, styrene or cyclohexene.[6]

TABLE I

THE REACTION OF PROPYLENE WITH A MIXTURE OF IODINE AND PERACETIC ACID IN ACETIC ACID–ETHER TO FORM 1-IODO-2-ACETOXYPROPANE

| $I_2$, mole | $CH_3CO_3H$, mole | Added material, mole | $CH_3CH{=}CH_2$, mole | Temp, °C | Yield, %[a] |
|---|---|---|---|---|---|
| 0.15 | 0.40 | ... | 0.8 | 20–40 | 53.7[b] |
| 0.15 | 0.27 | ... | 3.9 | 16–19 | 80.4 |
| 0.015 | 0.023 | *c* | 0.4 | 26–38 | 54.8 |
| 0.03 | 0.046 | *c* | 0.6 | 24–35 | 70.0 |
| 0.15 | 0.23 | $H_2O$ (1.0) | 0.6 | 23–37 | 41.9 |

[a] Yield based on iodine used. [b] Reaction time 16 days. The product composition was 1-iodo-2-acetoxypropane:1,2-diacetoxypropane = 80:20. [c] Irradiated by ultraviolet light from a 100-w mercury lamp at a distance of 10 cm.

In the absence of peracetic acid, iodine in an ether–acetic acid solution reacts with propylene to form 1,2-diiodopropane (*ca.* 55%) together with a small amount of 1-iodo-2-acetoxypropane. The reaction leads to an equilibrium (eq 1),[14] when *ca.* 85% iodine is consumed.

$$CH_3CH{=}CH_2 + I_2 \xrightleftharpoons{\text{acetic acid–ether}} CH_3CHI{-}CH_2I \quad (1)$$

The rate of halogen addition to olefin in acetic acid is second order in halogen[15–17] and hence the addition probably proceeds *via* an attack of molecular halogen on a halogen atom in a halogen–olefin complex,[18,19] forming cyclic halonium ion or carbonium ion. The addition may often be accompanied by haloacetate.[20,21]

As is obvious from kinetic data (Table II), the iodine addition under these conditions is little affected by ultraviolet radiation,[22] but is accelerated by the addition of sulfuric acid.

It is of interest to note that the rate of addition of iodine to propylene is faster than the reaction of iodine with peracetic acid, but is slower than the rate of iodoacetoxylation reaction of olefin with a mixture of iodine and peracetic acid (Table II). Hence, the rate-determining step is different from that of the reaction of benzene[2–4] with a mixture of iodine and peracetic acid, where the reaction of iodine with peracetic acid forming acyl hypohalite is rate-determining. Further, iodic acid, which was observed as precipitate in the reaction of benzene, is not detected in the olefin reaction.

TABLE II

SECOND-ORDER RATE CONSTANTS IN ACETIC ACID AT 30°

A. Reaction of Propylene with $I_2$ to Form $CH_3CHI{-}CH_2I$

| $[CH_3CH{=}CH_2]$, *M* | $[I_2]$, *M* | $k_2$ ($M^{-1}$ min$^{-1}$)[a] |
|---|---|---|
| 0.13 | 0.00516 | 0.01 |
| 0.23 | 0.0120 | 0.02 |
| 0.23 | 0.0120 | 0.04[b] |
| 0.21 | 0.0235 | 0.03 |
| 0.22 | 0.0240 | 0.04[c] |
| 0.21 | 0.0252 | 0.04 |
| 0.15 | 0.0500 | 0.11 |

B. Reaction of Propylene and $CH_3CO_3H$ to Form Epoxide

| $[CH_3CH{=}CH_2]$ | $[CH_3CO_3H]$ | $k_2$[d] |
|---|---|---|
| 0.24 | 0.132 | 0.005 |
| 0.28 | 0.230 | 0.005 |

C. Reaction of $I_2$ and $CH_3CO_3H$ to Form $HIO_3$

| $[I_2]$ | $[CH_3CO_3H]$ | $k_2$[e] |
|---|---|---|
| 0.0500 | 0.123 | 0.012 |
| 0.0528 | 0.230 | 0.011 |

D. Reaction of $CH_3CHI{-}CH_2I$ with $CH_3CO_3H$

| $[CH_3CHI{-}CH_2I]$ | $[CH_3CO_3H]$ | $k_2$ |
|---|---|---|
| 0.162 | 0.123 | 0.19 |

E. Reaction of $CH_3CH(OCOCH_3){-}CH_2I$ with $CH_3CO_3H$

| $[CH_3CH(OCOCH_3){-}CH_2I]$ | $[CH_3CO_3H]$ | $k_2$[f] |
|---|---|---|
| 0.10 | 0.132 | 0.1 |
| 0.096 | 0.040 | 0.1 |

F. Reaction of Propylene with $I_2$ and $CH_3CO_3H$

| $[CH_3CH{=}CH_2]$ | $[I_2]$ | $[CH_3CO_3H]$ | $k_2$[g] |
|---|---|---|---|
| 0.22 | 0.0250 | 0.0249 | 2 |
| 0.20 | 0.0240 | 0.0460 | 4 |
| 0.25 | 0.0120 | 0.0102 | 3 |

[a] Although the addition of iodine to olefin is expressed as $v = k_3[\text{olefin}][I_2]^2$, the second-order rate coefficient is calculated for comparison. [b] $H_2SO_4$ (0.19 *M*) was added. [c] Irradiated by ultraviolet light from a 100-w mercury lamp at a distance of 10 cm. [d] $k_2 = 0.0042$ at 25.8°. D. Swern, *Chem. Rev.*, **45**, 49 (1949). [e] $k_2 = 0.075$ at 50°. See ref 2. [f] Second-order rate coefficients decreased with time. The reactions D and E liberated iodine equimolar to consumed peracetic acid. [g] The third-order rate, $v = k_3[\text{olefin}][I_2][CH_3CO_3H]$, should be applied to the reaction, but the second-order coefficient from $v = k_2[\text{olefin}][I_2]$ is calculated for comparison. The coefficient decreased with time. The rates were too rapid to measure accurately.

In view of these facts, the following mechanism

$$CH_3CO_3H + I_2 + CH_3CO_2H \longrightarrow 2CH_3CO_2I + H_2O \quad (2)$$

$$CH_3CH{=}CH_2 + CH_3CO_2I \longrightarrow CH_3CH(OCOCH_3){-}CH_2I \quad (3)$$

is less probable as a principal pathway.

It was observed that 1,2-diiodopropane reacted with peracetic acid yielding 1-iodo-2-acetoxypropane (11%) and liberating iodine equimolar to reacted peracetic acid.

Reaction steps 4–6, however, do not seem to constitute a main process in the present reaction (iodoacetoxylation), since the rate of eq 4 as well as the

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(14) P. W. Robertson, *J. Chem. Soc.*, 2191 (1950).

(15) N. J. Bythell and P. W. Robertson, *ibid.*, 179 (1938).

(16) P. B. D. de la Mare, *Quart. Rev.* (London), **3**, 126 (1949).

(17) G. Williams, *Trans. Faraday Soc.*, **37**, 749 (1941).

(18) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt Co., New York, N. Y., 1959, p 520.

(19) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 202.

(20) G. Sumrell, R. G. Howell, B. M. Wyman, and M. C. Harvey, *J. Org. Chem.*, **30**, 84 (1965).

(21) K. Nozaki and R. A. Ogg, *J. Am. Chem. Soc.*, **64**, 709 (1942).

(22) F. G. Caughley and P. W. Robertson, *J. Chem. Soc.*, 1323 (1933).

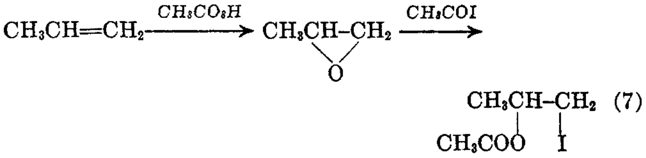
$$CH_3CHI\text{-}CH_2I + CH_3CO_3H \longrightarrow CH_3CH(OCOCH_3)\text{-}CH_2I + HOI \quad (4)$$

$$HOI + CH_3CO_3H \longrightarrow CH_3CO_2I + H_2O \quad (5)$$

$$CH_3CO_2I + CH_3CHI\text{-}CH_2I \longrightarrow CH_3CH(OCOCH_3)\text{-}CH_2I + I_2 \quad (6)$$

rate of iodine addition to propylene (eq 1) is slower than the three component reaction of propylene–iodine–peracetic acid (Table II).

Another mechanism involving the epoxidation of olefin followed by the reaction of epoxide with acetyl iodide[8] to form 1-iodo-2-acetoxypropane (eq 7 below)



$$CH_3CH{=}CH_2 \xrightarrow{CH_3CO_3H} CH_3CH\text{-}CH_2(O) \xrightarrow{CH_3COI} CH_3CH(OCOCH_3)\text{-}CH_2I \quad (7)$$

is improbable, since there is no indication of the formation of acetyl iodide in the present reaction and also the rate of epoxidation is very slow (Table II). It was observed that the reaction of propylene with peracetic acid in acetic acid gave 1,2-diacetoxypropane in 24% yield. This product was virtually absent in the iodoacetoxylation. Hence the product of iodoacetoxylation cannot be a mixture of diiodo- and diacetoxypropanes.

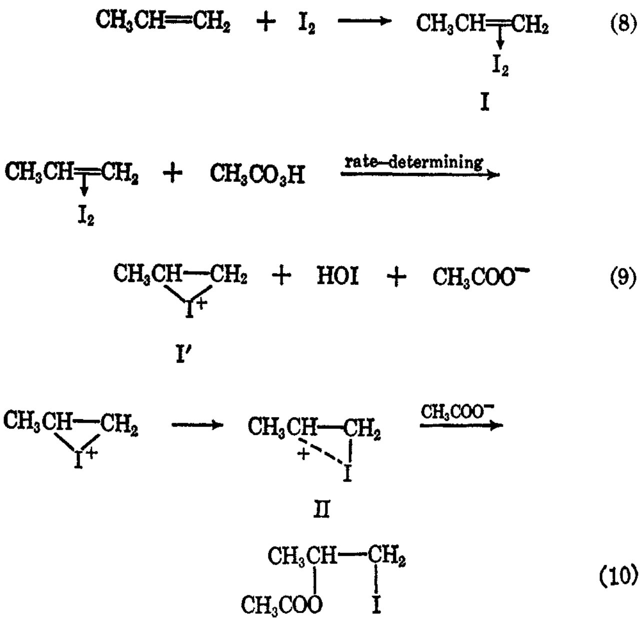
Although the sulfuric acid-catalyzed reaction of propylene with iodine in acetic acid also gave 1-iodo-2-acetoxypropane, the reaction required a very long time and the yield was very poor; hence, this course cannot be important.

It was also observed that 1-iodo-2-acetoxypropane reacted with peracetic acid liberating iodine equimolar to the peracetic acid consumed. This reaction, however, is not important, since the rate is slow and the product of this reaction, 1,2-diacetoxypropane, was virtually absent in the iodoacetoxylation.

Since no effect was observed on ultraviolet irradiation and no peroxide effect by peracetic acid is operative in view of the product structure, a radical chain mechanism is not conceivable for the iodoacetoxylation.

These observations lead to a mechanism involving a rapid complex formation between olefin and iodine[23] followed by a rate-determining attack of peracetic acid on the π complex I.

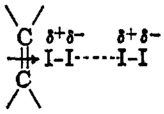
The initially formed π complex I between molecular iodine and olefin may be converted to a cyclic iodonium ion I′ and/or to a carbonium ion II by the abstraction of iodide ion, eq 9; the iodide ion is oxidized rapidly by peracetic acid to hypoiodic acid. Carbonium ion II reacts with acetate ion to form 1-iodo-2-acetoxypropane, eq 10. The rapid oxidation of iodide ion suppresses the formation of diiodide, eq 1, *i.e.*, an addition product of iodide ion to the carbonium ion. The carbonium ion II is more stabilized than $CH_3CHICH_2^+$ because of the greater possibility of delocalization of positive charge; hence, the product is not the 1-acetoxy but 2-acetoxy compound. The abstracted iodide ion may be converted by peracetic acid to acetyl hypoiodite which may rather slowly add to olefin.



$$HOI + CH_3COOH \longrightarrow CH_3COOI + H_2O \quad (11)$$

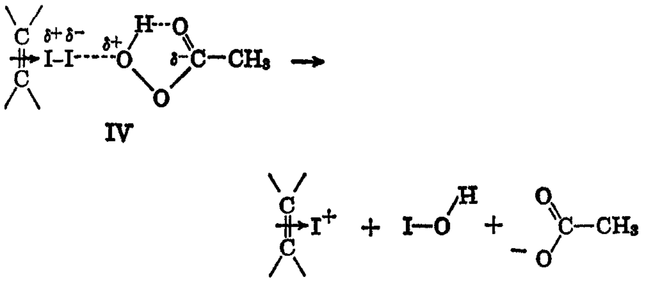
$$CH_3CH{=}CH_2 + CH_3COOI \longrightarrow CH_3CH(OCOCH_3)\text{-}CH_2I \quad (12)$$

As mentioned above, the addition of halogen to olefin in acetic acid is usually second order with halogen, hence the addition may proceed by a rate-determining attack of polarized halogen on the olefin–halogen π complex as illustrated in structure III.



III

The peracid seems to have an electrophilic oxygen atom because of the observed acid catalysis and the substituent effect (negative ρ- value) in the epoxidation of olefins with peracid.[24] Therefore, transition state IV for the iodoacetoxylation is suggested, where the polarized iodine molecule in the π complex may be abstracted by the peracid oxygen atom to give hypoiodic acid. Both transition states III and IV are analogous in a sense that heterolytic splitting of iodine in the π complex occurs.



IV

The rate data may also be explained by assuming a rapid and reversible formation of a peracetic acid–

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[23] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 458 (1952).

[24] Y. Ogata and I. Tabushi, *ibid.*, **83**, 3440, 3444 (1961).

iodine complex which slowly attacks olefin, but the presence of such a complex as well as its attack on olefin is difficult to consider. Another machanism which fits the rate equation is an attack of halogen on a π complex of olefin–peracid rapidly formed. The mechanism, however, is improbable because the rate of epoxidation with peracid is rather slow and no reasonable π complex is conceivable between peracid and olefin which may be attacked by halogen molecule to form the observed product.

# The Structure of Psilostachyin C, a New Sesquiterpene Dilactone from *Ambrosia psilostachya* DC.

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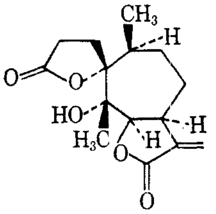
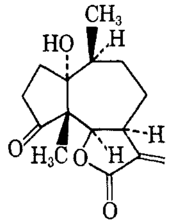
The structure of psilostachyin C, a new sesquiterpene dilactone from *Ambrosia psilostachya* DC., is shown to be **13**. Psilostachyin C was also isolated from *A. peruviana* Willd. and *A. deltoidea* (Torr.) Payne. Xantomicrol and damsin were also found in the last species.

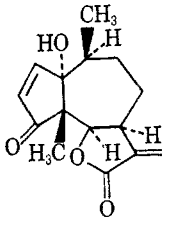
We previously reported the structure of psilostachyin[5,6] (**1**), $C_{15}H_{20}O_5$, the major sesquiterpene lactone isolated from a Galveston Island, Texas, collection of the *Compositae* species, *Ambrosia psilostachya* DC. Two other sesquiterpene lactones, psilostachyin B, $C_{15}H_{18}O_4$, and psilostachyin C, $C_{15}H_{20}O_4$, were found in the Galveston Island material. Coronopilin[7,8] (**2**), parthenin[8] (**3**), and ambrosiol[8] (**4**) are the only other sesquiterpenes isolated from other collections of *A. psilostachya.* We now describe the structure determination of psilostachyin C and its synthesis from damsin (**12**), a sesquiterpene lactone of known structure.



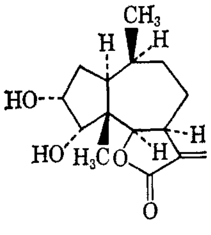
**1**



**2**



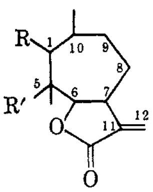
**3**



**4**

Psilostachyin C, $C_{15}H_{20}O_4$, mp 223–225°, $[\alpha]^{24°}{}_{D}$ −82 (*c* 0.6, $CHCl_3$), exhibited infrared (1775 and 1660 $cm^{-1}$) and ultraviolet ($\lambda_{max}$ 210 mμ, ε 10,150) spectra typical for an α,β′-unsaturated γ-lactone of the type found in the other sesquiterpene lactones, **1**–**4**, already described from *A. psilostachya.* A second infrared carbonyl absorption (1730 $cm^{-1}$) corresponded to the absorption expected for either a δ-lactone group or a cyclopentanone ring. That psilostachyin C did not contain either a keto or a hydroxyl group was shown by the absence of ultraviolet absorption and Cotton effect characteristic of ketonic chromophores and our failure to observe signals typical of hydroxyl proton when the nmr spectrum of psilostachyin C was run in deuterated dimethyl sulfoxide.[6,9]

The nmr spectrum of psilostachyin C in $CDCl_3$ provided further evidence for an α,β′-unsaturated γ-lactone system of the type found in **1**–**4**; a doublet at 4.70[10] ($J$ = 9 cps) was ascribed to the $C_6$ lactonic proton in **5** spin-coupled to one proton. Moreover, doublets ($J$ = 3 cps) at 5.50 and 6.22 were typical for the two vinyl protons belonging to a methylene group attached to $C_{11}$. The nmr spectrum also displayed signals characteristic for one tertiary (1.27, singlet) and one secondary methyl group (1.02, doublet, $J$ = 7 cps). Considering that **1** and psilostachyin C are found together in the same plant, the spectroscopic findings suggest partial formula A for psilostachyin C.



A

Evidence in addition to the infrared carbonyl absorption at 1730 $cm^{-1}$ to support the presence of a δ-lactone group in psilostachyin C was provided by the following reactions. When psilostachyin C was treated with a methanolic solution of benzaldehyde and sodium methoxide, a crystalline derivative, **6** (Scheme I),

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(3) Florida State University. Paper V in a series "Constituents of *Ambrosia* and Related Species" from the Department of Chemistry, The Florida State University. Paper IV: W. Herz, H. Chikamatsu, and L. R. Tether, *J. Org. Chem.*, **31**, 1632 (1966).

(4) To whom inquiries should be addressed.

(5) H. E. Miller, H. B. Kagan, W. Renold, and T. J. Mabry, *Tetrahedron Letters*, **No. 38**, 3397 (1965).

(6) T. J. Mabry, H. E. Miller, H. B. Kagan, and W. Renold, *Tetrahedron*, in press.

(7) (a) W. Herz and G. Högenauer, *J. Org. Chem.*, **26**, 5011 (1961); (b) T. A. Geissman and R. J. Turley, *ibid.*, **29**, 2553 (1964).

(8) T. J. Mabry, W. Renold, H. E. Miller, and H. B. Kagan, *ibid.*, **31**, 681 (1966).

(9) O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

(10) All chemical shift values are reported in parts per million (δ scale).