B. Triphenylphosphine–Carbon Tetrachloride Method.[9]—(*R*)-(−)-5-Hexen-2-ol (2.0 g), $[\alpha]^{25}D$ −13.7° (ether), triphenylphosphine (8.0 g), and carbon tetrachloride (16.0 g) were refluxed for 2.5 hr. After cooling to room temperature, the mixture was diluted with pentane to precipitate most of the phosphorus compounds, filtered, and distilled to give 0.95 g (40%) of 5-chloro-1-hexene, identified by the nmr spectrum: bp 118–121°; $[\alpha]^{25}D$ +29.4° (ether). The PCl_5 reaction with 5-hexen-2-ol of the same optical purity would give a chloride with a specific rotation of $[\alpha]^{25}D$ +38.9° (ether).

C. $SOCl_2$ Method.—Thionyl chloride (1.7 g) was added dropwise to a solution of (−)-5-hexen-2-ol (1.27 g), $[\alpha]^{25}D$ −13.7° (ether), in anhydrous pyridine (1.2 g) and 3 ml of anhydrous ether. The mixture was refluxed for 5.5 hr. Ice and water were added, and the ether layer was separated, washed, and dried. It had a positive rotation; according to the nmr spectrum it contained 5-chloro-1-hexene, some elimination product, and pyridine. (The latter are not optically active, and therefore do not contribute to the rotation.)

Reaction of (*R*)-(−)-2-Brosyloxy-5-hexene with Lithium Chloride.[8]—(*R*)-(−)-2-Brosyloxy-5-hexene (1.2 g), $[\alpha]^{25}D$ −8.43° (ether), lithium chloride (0.8 g), and 30 ml of ethanol (95%) were refluxed on a steam bath for 24 hr. After diluting with 10 ml of water, the solution was extracted with three portions of petroleum ether. The combined extracts were dried and concentrated to about 2 ml; this solution was composed largely of 5-chloro-1-hexene (nmr); assuming 100% yield for the conversion of the brosylate into the chloride, it had a specific rotation of $[\alpha]^{25}D$ +42.7°.

4-Chloropentan-1-ol. A. Ozonolysis in Ether and Reduction with Lithium Aluminum Hydride.—(*R*)-(−)-5-Chloro-1-hexene (4.1 g), $[\alpha]^{25}D$ −43.3° (ether), in 50 ml of anhydrous ether was ozonized at −70° until the blue color of excess ozone appeared. The solution was flushed with dry nitrogen and then added dropwise to a stirred mixture of lithium aluminum hydride (2.8 g) in 100 ml of anhydrous ether. After stirring at room temperature for 45 min, the excess of lithium aluminum hydride was destroyed by dropwise addition of a saturated aqueous solution of sodium tartrate. The precipitate was filtered over celite; the clear filtrate was dried over Molecular Sieves 4A, concentrated, and distilled, giving 2.286 g (54%) of (−)-4-chloropentan-1-ol: bp 70–75° (4.25 mm) [lit. bp 78–80° (10 mm),[14a] 76–77° (9 mm),[14b] 77–79° (10 mm);[14c] $n^{25}D$ 1.4454 (lit. $n^{20}D$ 1.4503,[14b] $n^{20}D$ 1.4490[14c]); $[\alpha]^{25}D$ −35.5° (ether); ir, 3340 (OH), 1050 (primary alcohol), 660 cm^{-1} (C–Cl); nmr ($CDCl_3$), 1.50 (d, 3, J = 6.5 Hz, methyl), *ca.* 1.75 (m, 4), *ca.* 3.6 (m, 2, $-CH_2-OH$), *ca.* 4.0 (m, 1), 4.82 (s, 1, OH).

Using different solvents (chloroform, methanol, ethanol) and reducing with sodium borohydride gave less satisfactory results.

B. *Via* γ-Chlorovaleraldehyde.—5-Chloro-1-hexene (2.0 g of racemic material) in 50 ml of anhydrous methanol was ozonized at −70°. The solution of the ozonide was reduced by adding 2 ml of dimethyl sulfide at −15° and working up according to the procedure of Pappas, *et al.*[12] Distillation of the product gave 0.585 g (29%) of γ-chlorovaleraldehyde: bp 65–75° (11 mm) [lit.[27] bp 70–71° (16 mm)]; purity *ca.* 90% (vpc); ir, 3450 (overtone), 2820 and 2720 (–CHO), 1725 (C=O), 660 (C—Cl); nmr ($CDCl_3$), 1.52 (d, 3, J = 6.5 Hz, methyl), *ca.* 2.0 (m, 2), *ca.* 2.6 (m, 2), *ca.* 4.0 (m, 1), 9.65 (t, 1, J = 1 Hz, CHO).

To a solution of 0.386 g of this product in a mixture of 10 ml of dioxan and 5 ml of water was added 4.5 g of sodium borohydride. After stirring at room temperature for 1 hr, dilute HCl was added, and the alcohol was extracted with five portions of ether. The combined extracts were dried and distilled, giving 0.309 g (79%) of 4-chloropentan-1-ol, bp 76–81° (10 mm), identical with the product of the above reaction according to infrared and vpc data.

Attempts to get a better yield of γ-chlorovaleraldehyde using the tetracyanoethylene method[13] were unsuccessful.

(*R*)-(−)-2-Chloro-5-methoxypentane.—A solution of diazomethane (prepared from 25 g of N-methyl-N-nitroso-N′-nitroguanidine) in 200 ml of methylene chloride was dropwise added at about −30° to a stirred solution of (*R*)-(−)-4-chloropentan-1-ol (1.8 g), $[\alpha]^{25}D$ −35.5° (ether), and *ca.* 160 mg of HBF_4 (*ca.* 60%) in 10 ml of ether and 10 ml of methylene chloride. After stirring at 0° for 1 hr the solution was colorless. The small amount of amorphous polymethylene was filtered off, and the solution was extracted with three portions of saturated aqueous potassium hydrogen carbonate solution and three portions of sodium chloride solution, dried, and distilled yielding 0.58 g (30%) of (*R*)-(−)-2-chloro-5-methoxypentane: bp 52–55° (12 mm); $[\alpha]^{25}D$ −32.1° (ether); ir, 2710 (OCH_3), 1110 (ether), 660 cm^{-1} (C-Cl); nmr (CH_2Cl_2), 1.40 (d, 3, J = 6.5 Hz, methyl), *ca.* 1.65 (m, 4), 3.23 (s, 3, methoxy), *ca.* 3.3 (m, 2, $-CH_2-OCH_3$), *ca.* 4.0 (m, 1).

Anal. Calcd for $C_6H_{13}OCl$: C, 52.75; H, 9.59; Cl, 25.96. Found: C, 52.53; H, 9.57; Cl, 26.24.

Registry No.—**4,** 17397-23-8; **5,** 17397-24-9; **6,** 17397-25-0; **7,** 17397-26-1; (*S*)-2-brosyloxy-5-hexene, 17397-27-2; Δ^5-2-hexenyl hydrogen phthalate, 17408-12-7; (+)-Δ^5-2-hexene hydrogen phthalate, 17397-28-3; (−)-5-hexen-2-ol, 17397-29-4; γ-chlorovaleraldehyde, 17408-13-8.

(27) B. Helferich and W. Dommer, *Chem. Ber.*, **53**, 2009 (1920).

The Acetylation of Phenylcyclopropane[1]

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Received April 1, 1968

Reaction of phenylcyclopropane with acetyl chloride–aluminum chloride at 0–5° affords not only *p*-cyclopropylacetopheone (**6**, 78%) but also 1-(4′-acetylphenyl)-2-chloropropane (**3**, 17%). The alkene 1-(4′-acetylphenyl)propene (**7**) is shown not to be an intermediate in the acylation, although **7** can be prepared in good yield from **6** and 80% aqueous sulfuric acid. The minor product **3** may be formed during the acylation from an intermediate such as **5** *via* a hydride shift.

It was recently shown that the products obtained from acetylation of cyclopropane with acetyl chloride and aluminum chloride cannot be accounted for by a conventional carbonium ion mechanism, but are easily rationalized *via* protonated cyclopropanes.[3] On the other hand, acetylation of 1,1-dimethylcyclopropane proceeds by initial isomerization to 2-methyl-2-butene, followed by conventional electrophilic acetylation of the alkene. Methylcyclopropane occupies an intermediate position and the acetylation products can be rationalized either by protonated cyclopropanes or by a combination of two more conventional schemes, a clear choice not yet being possible.

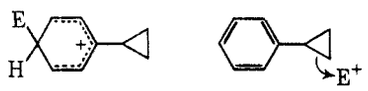
In this paper consideration is given to the acetylation of phenylcyclopropane, which can in principle undergo electrophilic attack at either the phenyl or the cy-

(1) This research was supported by grants from the National Institutes of Health and the National Science Foundation, for which the authors express their appreciation.

(2) National Institutes of Health Predoctoral Fellow at Michigan State University, 1967–1968.

(3) For a preliminary communication, see H. Hart and R.H. Schlosberg, *J. Amer. Chem. Soc.*, **88**, 5030 (1966); for a full account with additional information, see *ibid.*, **90**, 5189 (1968).

clopropyl ring. It might be expected that the phenyl ring would be activated, relative to benzene, especially to electrophilic attack *para* (or *ortho*) to the cyclopropyl substituent, because of the well-known stabilizing effect of the cyclopropane ring on neighboring positive carbon (as in transition state **1**). The expectation with regard to attack on the cyclopropane ring is less clear-cut. Inductively the phenyl group should be elec-



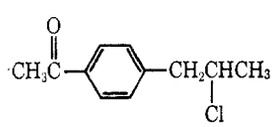
1 **2**

E = electrophile

tron withdrawing, and thus decrease the susceptibility of the cyclopropane ring to electrophilic attack, but, if attack were to proceed as in **2**, the resulting ion would be benzylic, suggesting that phenylcyclopropane might be more easily attacked than cyclopropane itself.

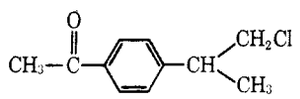
Prior work shows that it is the phenyl ring which wins out. Hart and Levitt[4] obtained a 48% yield of *p*-cyclopropylacetophenone from the Friedel–Crafts acetylation of phenylcyclopropane. In addition, 10% of a minor product whose structure was not elucidated was also formed. When the reaction was run at −75°, the yield of *p*-cyclopropylacetophenone was reported[5] to be 90%.

To determine whether the minor product referred to above was due to acetylation of the cyclopropane ring, and to seek other volatile products if present, we reinvestigated the acetylation of phenylcyclopropane, taking advantage of techniques not previously[4] available. When phenylcyclopropane was acetylated in methylene chloride at 0° for 1 hr, two volatile products (vpc) were obtained in 78 and 17% yield, respectively. The former was *p*-cyclopropylacetophenone (**6**), as shown by the identity of its melting point, retention time, and ir, uv, and nmr spectra with those of an authentic sample.[6] The minor product is considered to be 1-(4′-acetylphenyl)-2-chloropropane (**3**) on the basis of the following evidence. The ir spectrum showed an aromatic carbonyl absorption at 1685 cm^{-1} and a carbon–chlorine stretching band at 752 cm^{-1}.



3

The uv spectrum was nearly identical with that of *p*-methylacetophenone,[7] with λ_{max}^{EtOH} at 250 mμ (log ε 4.11), indicating that the compound was a *p*-alkylacetophenone. The nmr spectrum requires the assigned structure. The aromatic protons constituted an A_2B_2 system centered at τ 2.25 and 2.87 (J = 8.5 Hz), as required by the *para* substitution. In addition there was a sharp three-proton signal at τ 7.51 (methyl ketone), a two-proton doublet at 6.98 (J = 7.2 Hz) for the benzylic methylene group, a multiplet centered at 5.85 for the methine proton, and a doublet at 8.52 (J = 7.2 Hz) for the remaining methyl group. The alternative structure **3′** would give the same splitting pattern (a doublet for the methylene and –CH–CH_3 groups and a multiplet for the methine proton). Structure **3′** can be eliminated, however, on chemical-shift grounds, as seen in Table I.



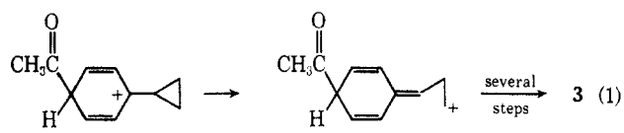
3′

TABLE I
PREDICTED AND OBSERVED CHEMICAL SHIFTS FOR THE MINOR ACETYLATION PRODUCT OF PHENYLCYCLOPROPANE

Group	Predicted[a] chemical shift, τ Structure **3**	Structure **3′**	Observed chemical shift, τ
CH	5.63–5.98	7.11	5.85
CH_2	6.80–7.06	6.25	6.98

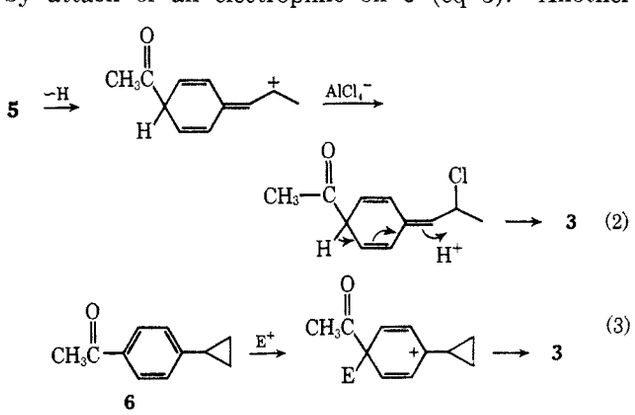
[a] Based on values in L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Ltd., London, 1959, pp 53–58.

It is thus clear that both products (95% yield altogether) are derived from acetylation of the phenyl ring, but the mechanism by which **3** is formed is uncertain. Several alternatives are possible. The cyclopropane ring opening may occur during the electrophilic substitution (**4** → **5**) (eq 1) or the major reaction product, *p*-cyclopropylacetophenone (**6**), may undergo subsequent ring opening.



4 **5** (1)

Several experiments were performed to test the latter alternative. Compound **6** was recovered unchanged from treatment with aluminum chloride in methylene chloride at 0° for 1 hr and from attempted acetylation at 5° for 25 min, but acetylation of **6** at 38° for 1 hr gave a small yield (15%) of **3**, and this was increased to 50% after 24 hr. Thus it does seem as if **6** may be the precursor of **3**, or may be transformed into a precursor of **3** under acetylation conditions. For example, the path from **5** → **3** could involve hydride transfer from the intermediate in the first acetylation (**5**) (eq 2). A similar intermediate could be produced by attack of an electrophile on **6** (eq 3). Another



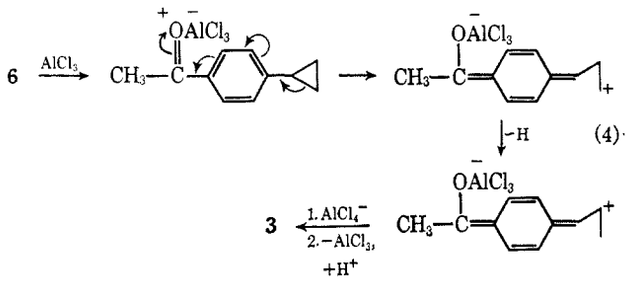
(2) (3)

6

E = H^+ or CH_3CO^+

(4) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).
(5) R. Ya. Levina and P. A. Gembitskii, *J. Gen. Chem. USSR*, **31**, 3242 (1961); R. Ya. Levina, P. A. Gembitskii, V. N. Kostin, S. M. Shostakovskii, and E. G. Treshchova, *ibid.*, **33**, 365 (1963).
(6) This remained from our previous study.[4]
(7) R. B. Turner and D. M. Voitle, *J. Amer. Chem. Soc.*, **73**, 1403 (1951).

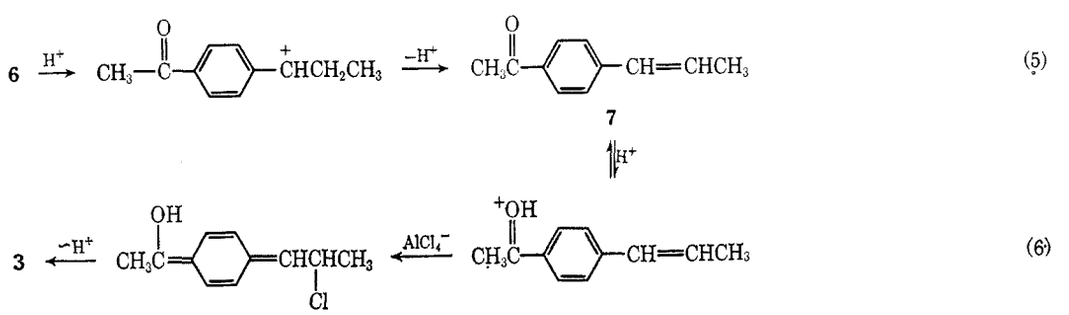
possibility is coordination of the Lewis acid with the carbonyl group of **6** (eq 4), although this reaction does not occur with aluminum chloride alone at 0° (1 hr).



(4)

Still other possibilities include the isomerization of either phenylcyclopropane or **6** under acid conditions to the corresponding allyl isomers, followed by addition of HCl to the double bond. In fact, as seen below, **6** does isomerize in acid, but to a propenylbenzene rather than an allylbenzene.

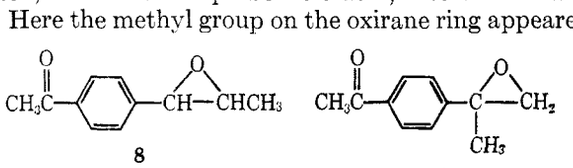
Even the isomerization of **6** to the alkene **7** (eq 5) followed by Michael-type addition of HCl to the double bond could lead to the observed product **3** (eq 6). Strangely, it was not previously known



(5) (6)

whether additions of HCl to **7** would follow the Michael orientation or a benzyl cation path, which would give the 1-chloro isomer.

Compound **7**, previously unknown, was prepared in high yield by treatment of **6** with 80% aqueous sulfuric acid. Its structure was reasonably clear from spectral data. The ultraviolet absorption at 286 mμ is similar to that (280 mμ) for *p*-acetylstyrene[8] and the ir spectrum showed both C=O and C=C (1680, 1650, 1603 cm^{-1}). The nmr spectrum showed a multiplet centered at τ 3.75 for the two vinyl protons, and an allylic methyl group at 8.14, also as a multiplet apparently split by both vinyl protons. To confirm that the side chain was propenyl and not isopropenyl, **7** was converted, with *m*-chloroperbenzoic acid, into the oxirane **8**. Here the methyl group on the oxirane ring appeared

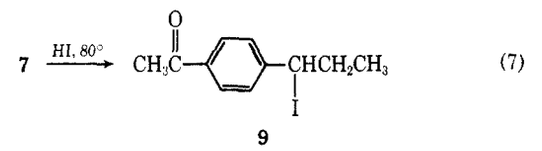


8 **8′**

as a doublet at τ 8.70 (J = 5.4 Hz); had the side chain been isopropenyl, this methyl would not have been split (see **8′**). The other spectral data (see Experimetal Section) are consistent with structure **8**.

It was found that compound **7** did not add hydrogen chloride under a variety of conditions which approximate those of the acylation reaction. It was recovered unchanged from treatment with acetyl chloride–aluminum chloride in methylene chloride at 5° and from treatment with hydrogen chloride, either alone or with aluminum chloride present, at room temperature. Finally, when **7** was initially added to an acylation of phenylcyclopropane, there was no increase in the yield ratio of **3** to **6** and over 50% of the added **7** survived the reaction.

Under forcing conditions it was possible to add hydrogen iodide to **7**. The product was **9** (and not the iodo analog of **3**) (eq 7) showing that addition to **7**



(7)

9

followed the path to be expected from an intermediate benzyl cation, rather than a Michael addition path. The structure of **9** is clear from its nmr spectrum (see Experimental Section).

It is concluded that **7** cannot be an intermediate in the formation of **3**, and that **3** is probably formed during the acylation of phenylcyclopropane by a hydride shift from an intermediate such as **5**.

Experimental Section[9]

Acetylation of Phenylcyclopropane.—A solution of 1.57 g (0.02 mol) of acetyl chloride in 6 ml of methylene chloride was added dropwise at 5° to a suspension of 2.66 g (0.02 mol) of anhydrous aluminum chloride in 6 ml of methylene chloride and the mixture was stirred until homogeneous (10 min). At the same temperature, a solution of 2.56 g (0.02 mol) of phenylcyclopropane in 12 ml of methylene chloride was added dropwise over 25 min. The mixture became cherry red. The reaction mixture was poured onto a mixture of 11 ml of concentrated hydrochloric acid and 100 g of ice, and the organic layer was washed (water, saturated sodium bicarbonate solution twice and water) and dried (sodium sulfate). The product was analyzed on a 5-ft 20% FFAP on Chromosorb W vpc column at 200° with a helium flow rate of 40 cc/min. The two major products, retention times of 7.4 and 15.8 min, accounted for 95% of the phenylcyclopropane, none of which was recovered. The major product (78%) with shorter retention time was *p*-cyclopropylacetophenone (**6**). Its nmr spectrum (CCl_4) consisted of an A_2B_2 pattern (4 H) at τ 2.10 and 2.73 (J = 8.5 Hz), a singlet at 7.42 (3 H), and multiplets at 8.07 (1 H) and 8.93 (4 H). Its ir and uv spectra were identical with those of an authentic sample.[4] The minor product (17%) was **1-(4′-acetylphenyl)-2-chloropropane** (**3**), bp 127–129° (2.8 mm). Its ir spectrum (liquid film) showed principal bands at 1685 ($\nu_{C=O}$), 1607 ($\nu_{C=C}$), and 752 cm^{-1} (ν_{C-Cl}). The nmr spectrum (CCl_4) consisted of an aromatic A_2B_2 system (J = 8.5 Hz) at τ 2.25 and at 2.87 (4 H), a sharp three-proton resonance at 7.51, a complex multiplet

(8) W. H. Saunders and R. A. Williams, *J. Amer. Chem. Soc.*, **79**, 3712 (1957).

(9) Analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

from 5.68 to 6.02, centered at 5.85 (1 H), a doublet (J = 7.2 Hz) at 6.98 (2 H), and a doublet (J = 7.2 Hz) at 8.52 (3 H). The uv spectrum (95% EtOH) showed λ_{max} 250 mμ (log ε 4.11).

Anal. Calcd for $C_{11}H_{13}OCl$: C, 67.17; H, 6.66; Cl, 18.03. Found: C, 67.28; H, 6.57; Cl, 18.11.

Treatment of *p*-Cyclopropylacetophenone with Aluminum Chloride.—To a solution of 0.250 g (0.0015 mol) of *p*-cyclopropylacetophenone (**6**) in 5 ml of methylene chloride at 0° was added 0.183 g (0.0015 mol) of aluminum chloride. The mixture was stirred for 1 hr at 0° and then poured onto a mixture of 1 ml of concentrated hydrochloric acid and 10 g of ice. The organic layer was washed successively with water, saturated sodium bicarbonate solution, and water and dried (magnesium sulfate). Removal of the solvent provided an oil which had ir and nmr spectral identical with those of the starting material.

Acetylation of *p*-Cyclopropylacetophenone.—A solution of 0.235 g (0.003 mol) of acetyl chloride in 3 ml of methylene chloride was added dropwise at 5° to a suspension of 0.4 g (0.003 mol) of anhydrous aluminum chloride in 3 ml of methylene chloride and the mixture was stirred until homogeneous. At the same temperature, a solution of 0.48 g (0.003 mol) of *p*-cyclopropylacetophenone in 8 ml of methylene chloride was added dropwise over 20 min. Stirring was continued for 5 min. The reaction mixture was poured onto a mixture of 2 ml of concentrated hydrochloric acid and 20 g of ice, and the organic layer was washed with water, saturated sodium bicarbonate solution, and water and dried (magnesium sulfate). Evaporation of the solvent provided an oil which had ir and nmr spectra identical with those of the starting material. Vpc also indicated that only starting material was recovered from the reaction.

A similar experiment at 38° for 1 hr gave (vpc analysis) 85% recovered *p*-cyclopropylacetophenone (**6**) and 15% of 1-(4′-acetylphenyl)-2-chloropropane (**3**). At 30° with 24-hr reaction time the products were 50% **6** and 50% **3**.

1-(4′-Acetylphenyl)propene (**7**).—To a solution of 1.0 g (0.0063 mol) of *p*-cyclopropylacetophenone (**6**) in 10 ml of methylene chloride was added over a 15-min period 15 ml of 80% aqueous sulfuric acid and the ensuing dark brown solution was stirred for an additional 15 min, then slowly poured onto 100 g of crushed ice. The organic layer was extracted with 50 ml of methylene chloride and dried over anhydrous sodium sulfate. After removal of the solvent *in vacuo*, 0.93 g (93%) of a pale yellow oil was obtained, which is assigned the structure of **1-(4′-acetylphenyl)-propene** (**7**), bp 90–92° (0.35 mm). It showed a single peak on vpc (5 ft × 0.25 in. 20% FFAP on Chromosorb W column, 210°, helium flow rate of 50 cc/min). The principal ir bands (liquid film) appeared at 1680 ($\nu_{C=O}$), 1650 ($\nu_{C=C}$), and 1603 cm^{-1} ($\nu_{C=C}$). The nmr spectrum (CCl_4) showed an A_2B_2 system centered at τ 2.33 and 2.84 (J = 8.4 Hz) for four protons, a 3 H multiplet centered at 8.14, a sharp 3 H singlet at 7.58, and a multiplet (2 H) centered at 3.75. The uv spectrum (95% EtOH) showed λ_{max} 286 mμ (compare with 280 mμ reported for *p*-acetylstyrene).[8] Compound **7** polymerized on prolonged standing at room temperature.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.39; H, 7.55.

2-(4′-Acetylphenyl)-3-methyloxirane (**8**).—To an ice-cold solution of 0.160 g (0.001 mol) of 1-(4′-acetylphenyl)propene in 10 ml of methylene chloride was added during 5 min a solution of 0.210 g (0.0011 mol) of *m*-chloroperbenzoic acid in 5 ml of methylene chloride. The mixture was stirred for 1.5 hr at ice-bath temperature, then for 22 hr at room temperature. Excess per acid was destroyed by adding 10% sodium sulfite until a test with starch–iodide paper was negative. The reaction mixture was washed successively with 5% sodium bicarbonate solution, water, and saturated sodium chloride solution and dried (magnesium sulfate). Removal of the solvent provided an oil which is assigned the structure of **2-(4′-acetylphenyl)-3-methyloxirane** (**8**), bp 95–96° (0.45 mm). It had principal ir bands (CCl_4) at 1685 ($\nu_{C=O}$) and 1612 cm^{-1} ($\nu_{C=C}$, aromatic). The nmr spectrum (CCl_4) consisted of a three proton doublet at τ 8.70 (J = 5.4 Hz), a sharp three proton singlet at τ 7.65, a quartet of doublets centered at τ 7.22 (J = 5.4 and 1.8 Hz) which integrated for one proton, a one proton doublet at τ 6.64 (J = 1.8 Hz) and an A_2B_2 system for four protons centered at τ 2.97 and τ 2.38 (J = 8.4 Hz).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.96; H, 6.90.

Attempted Acetylation of 1-(4′-Acetylphenyl)propene.—A solution of 0.23 g (0.003 mol) of acetyl chloride in 2 ml of methylene chloride was added dropwise at 5° to a suspension of 0.4 g (0.003 mol) of anhydrous aluminum chloride in 2 ml of methylene chloride and the mixture was stirred until homogeneous. At the same temperature, a solution of 0.5 g (0.003 mol) of 1-(4′-acetylphenyl)propene in 4 ml of methylene chloride was added dropwise over 15 min. The reaction mixture first became red and then dark green. Stirring was continued for 5 min. The reaction mixture was poured onto a mixture of 1 ml of concentrated hydrochloric acid and 10 g of ice, and the organic layer was washed with water, saturated sodium bicarbonate solution, and water and dried (magnesium sulfate). Evaporation of the solvent provided a yellow oil which had ir and nmr spectra identical with those of a starting material.

Attempted Reaction of 1-(4′-Acetylphenyl)propene with Hydrogen Chloride.—Hydrogen chloride was bubbled through a stirred solution of 0.5 g (0.003 mol) of 1-(4′-acetylphenyl)propene in 5 ml of methylene chloride at room temperature for 75 min. The yellow solution was diluted to 15 ml with additional methylene chloride, then washed with water, saturated sodium bicarbonate solution, and water and dried (magnesium sulfate). Evaporation of the solvent provided a yellow oil which had ir and nmr spectra identical with those of the starting material. An identical experiment but with 0.366 g (0.003 mol) of aluminum chloride also present in the reaction mixture again afforded only recovered starting material.

Acetylation of a Mixture of Phenylcyclopropane and 1-(4′-Acetylphenyl)propene.—A solution of 0.314 g (0.004 mol) of acetyl chloride in 3 ml of methylene chloride was added dropwise at 5° to a suspension of 0.532 g (0.004 mol) of anhydrous aluminum chloride in 3 ml of methylene chloride and the mixture was stirred until homogeneous. At the same temperature, a solution of 0.354 g (0.003 mol) of phenylcyclopropane and 0.160 g (0.001 mol) of 1-(4′-acetylphenyl)propene in 6 ml of methylene chloride was added dropwise over 20 min. The reaction mixture was poured onto a mixture of 2 ml of concentrated hydrochloric acid and 20 g of ice, and the organic layer was washed with water, saturated sodium bicarbonate solution, and water and dried (magnesium sulfate). Evaporation of the solvent provided a yellow oil. A comparison of the results from this experiment with data obtained from the acetylation of phenylcyclopropane indicated that no change in the ratio of 1-(4′-acetylphenyl)-2-chloropropane to *p*-cyclopropylacetophenone had occurred.

Addition of Hydrogen Iodide to 1-(4′-Acetylphenyl)propene.—1-(4′-Acetylphenyl)propene (420 mg, 0.00262 mol) was added to a mixture of 3.3 g (0.02 mol) of potassium iodide in 2.9 g (0.025 mol) of 95% orthophosphoric acid. The mixture was stirred and heated at 80° for 3 hr, which was then allowed to cool, and treated with 10 ml of water and 40 ml of ether with continued stirring. The ether extract was separated, decolorized with 10% aqueous sodium thiosulfate solution, washed with saturated sodium chloride solution, and dried (magnesium sulfate). The solvent was evaporated to provide an oil. Vpc investigation of this oil under two different sets of conditions (5 ft × 0.25 in. DEGS 60/80 Chromosorb W column, 180° 50 cc/min of helium, and 5 ft × 0.25 in. SE-30 column, 200, 60 cc/min of helium) showed the volatile portion of the oil to be 95% pure in one component. This compound, which is assigned the structure of **1-(4′-acetylphenyl)-1-iodopropane** (**9**), was vpc purified (SE-30 column). It showed ir bands (CCl_4) at 1683 ($\nu_{C=O}$) and 1611 cm^{-1} ($\nu_{C=C}$, aromatic). The nmr spectrum (CCl_4) consisted of a three-proton triplet at τ 9.08 (J = 7.7 Hz), a two-proton multiplet from 8.58 to 8.17, a sharp three-proton singlet at 7.53, a one-proton triplet at 7.38 (J = 7.8 Hz), and an A_2B_2 system for four protons centered at 2.93 and 2.31 (J = 8.4 Hz). The compound quickly turned purple and was too unstable to permit microanalysis.

Registry No.—Phenylcyclopropane, 873-49-4; **3**, 17417-02-6; **6**, 6921-45-5; **7**, 17417-03-7; **8**, 17448-09-8; **9**, 17417-04-8.