concentrated under reduced pressure, diluted with water, washed with ether, acidified, and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded 242 mg. of semi-crystalline material, m.p. 106–115°. Recrystallization from benzene yielded 124 mg. of colorless crystals, m.p. 121–123°. Five recrystallizations from benzene afforded 94 mg. of colorless microcrystals, m.p. 122–122.6°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.3; H, 8.80.

3(a)-Hydroxy-*trans*-decalyloxy-2(a)-acetic Acid Lactone (XV).—A solution of 200 mg. (0.88 mmole) of 3(a)-hydroxy-*trans*-decalyloxy-2(a)-acetic acid (m.p. 121–123°) and 75 mg. of *p*-toluenesulfonic acid monohydrate in 150 ml. of benzene was heated at reflux under nitrogen for 10 min.; the distillate was collected in a water separator. The solution was washed with 5% aqueous sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and concentrated to a yellow liquid (152 mg.) at room temperature under reduced pressure. Evaporative distillation at 100° (0.1 mm.) afforded 94.5 mg. (51% yield) of colorless crystals, m.p. 46.5–50°. Nine recrystallizations from petroleum ether (b.p. 37°) yielded colorless crystals, m.p. 51.8–52.5°.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; 8.58. Found: C, 68.3; H, 8.42.

Upon standing at room temperature in a tightly closed vial, the analytical sample gradually liquified.

3-Keto-*trans*-decalyloxy-2(a)-acetic Acid (XVI).—The method described by Jones[30] was used. A solution of 81 mg. (0.81 mmole) of chromium trioxide in 1.0 ml. of water and 0.3 ml. of sulfuric acid was added dropwise with stirring and ice-bath cooling to a solution of 200 mg. (0.88 mmole) of 3(a)-hydroxy-*trans*-decalyloxy-2(a)-acetic acid (m.p. 121–123°) in 4.0 ml. of acetone over a period of 30 min. After stirring for 1.5 hr. at room temperature, the mixture was poured into 100 ml. of water. The solution was extracted with ether. The ether solution was washed with saturated salt solution, dried over anhydrous magnesium sulfate, and concentrated to a colorless oil (218 mg.). Crystallization from petroleum ether–ether afforded 124 mg. (62% yield) of colorless crystals, m.p. 68–70°. Eleven recrystallizations yielded 42 mg. of colorless prisms, m.p. 69.5–70.5°.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.03. Found: C, 64.1; H, 8.17.

3-Keto-*trans*-decalyloxy-2(e)-acetic Acid (XVII).—A solution of 200 mg. (0.88 mmole) of crude 3-keto-*trans*-decalyloxy-2(a)-acetic acid and 100 mg. of sodium hydroxide in 20 ml. of water was heated at reflux under nitrogen for 2 hr. The solution was cooled, diluted with water, acidified, and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded 207 mg. of yellow crystals, m.p. 95–105°. Recrystallization from petroleum ether–ether yielded 125 mg. of colorless crystals, m.p. 107–113°. Repeated recrystallization failed to improve the melting point. Attempted chromatographic purification on silicic acid was unsuccessful. Paper chromatographic analysis, using a butanol–water system with brom cresol green solution for the detection of the spots, suggested that the product was contaminated with starting material.

3(e)-Hydroxy-*trans*-decalyloxy-2(e)-acetic Acid (XIX).—To a refluxing solution of 300 mg. (1.33 mmoles) of 3-keto-*trans*-decalyloxy-2(e)-acetic acid (m.p. 107–113°) in 50 ml. of anhydrous isopropyl alcohol was added in small portions over a period of 30 min., a total of 3.5 g. of sodium metal. The mixture was heated at reflux for 3 hr., then 50 ml. of methanol was added. The solution was poured onto 250 ml. of ice, acidified, and extracted with ether. The ether layers were washed with saturated salt solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent at room temperature under reduced pressure afforded 306 mg. of yellowish crystalline material. Recrystallization from benzene–methanol at 65° yielded 73.6 mg. of colorless crystals, m.p. 136–141°. Further purification was precluded by facile lactonization as indicated by the development of a band at 5.72 μ in the infrared spectrum.

3(e)-Hydroxy-*trans*-decalyloxy-2(e)-acetic Acid Lactone (XVIII).—Evaporative distillation at 100° (0.1 mm.) of the residue obtained from the concentration of the mother liquor from the preceding experiment afforded 75 mg. of colorless crystals, m.p. 92–112°, which was chromatographed on 2.7 g. of Florisil. The fraction eluted with benzene afforded 26 mg. of product, m.p. 111.5–112°. Recrystallization from petroleum ether (b.p. 68°) yielded colorless needles, m.p. 113.3–113.6°.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.58. Found: C, 68.3; H, 8.57.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Transmission of Electrical Effects Through Homoallylic Systems. IV. The Solvolysis of Some Secondary Cyclopropylcarbinyl *p*-Nitrobenzoates

BY RICHARD A. SNEEN AND ARTHUR L. BARON

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The *p*-nitrobenzoate esters of methyl-, phenyl- and *p*-tolylcyclopropylcarbinol have been solvolyzed in 60 volume per cent. aqueous acetone at various temperatures. The relative first-order rates of solvolysis at 65° were found to be k_{methyl} = 1, k_{phenyl} = 179 and $k_{p\text{-}tolyl}$ = 2140. These rates are contrasted with the recently reported[1b,c] rates of solvolysis of similarly substituted cholesteryl *p*-toluenesulfonates and the conclusion is drawn that the anomalously low rate of reaction of 6-phenylcholesteryl *p*-toluenesulfonate is accounted for neither by ground state energy nor by stereoelectronic considerations, but rather that it is a result of steric inhibition of resonance in the transition state.

Introduction

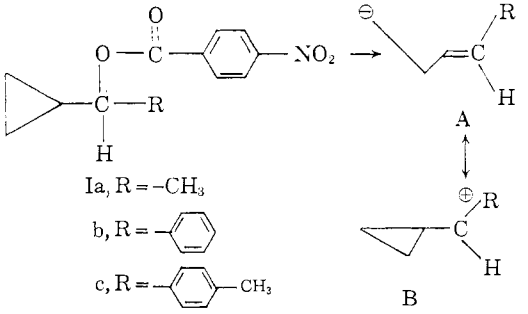
We recently reported the results of a series of experiments undertaken with a view toward determining the mechanisms by which electrical effects are transmitted through homoallylic systems.[1a,b,c] In particular the rates of solvolysis of some 6-substituted cholesteryl *p*-toluenesulfonates were measured in the solvent system 90 volume per cent. aqueous dioxane. The effect of 6-methyl substitution, a 75-fold rate enhancement, was interpreted as further confirmation of the generally accepted picture of electron delocalization in the cyclocholesteryl cation. However the kinetic effect of 6-aryl substitution contrasted sharply with this picture: even 6-*p*-anisylcholesteryl *p*-toluenesulfonate solvolyzed more slowly than the unsubstituted cholesteryl ester.

To explain this unusual order of reactivity, three factors were considered.[1c] First, it was suggested that the decreased reactivity of the aryl-substituted compounds results from the increased ground state stabilization of the starting esters due to the conjugation of the aryl rings with the C_5–C_6 π-electrons; it was also suggested that non-bonded steric

(1) (a) R. A. Sneen, THIS JOURNAL, **80**, 3971 (1958); (b) **80**, 3977 (1958); (c) **80**, 3982 (1958).

interactions between a planar aryl ring at C_6 and the approaching atoms of the incipient three-membered ring might result in steric inhibition of resonance in the transition state; and, finally, it was thought possible that effective conjugation of the π-orbitals of the aryl ring with the homoallylic cationic system might be stereoelectronically inhibited. Thus the distortion of the C_5–C_6 π-orbital during the formation of the cyclocholesteryl cation might be such as to prevent the aryl π-electrons from being transmitted to the electron-deficient area.

The work described in this paper was undertaken in an attempt to determine which, if any, of these factors is responsible for the unusual order of reactivities observed with the cholesteryl esters. We set out to synthesize a series of simple model compounds which on solvolysis would duplicate, as nearly as possible, the stereoelectronic features of the cyclocholesteryl ion, but whose transition states should be less subject to steric inhibition of resonance. The model systems chosen for this study were methyl- (Ia), phenyl- (Ib) and *p*-tolylcyclopropylcarbinyl *p*-nitrobenzoate (Ic). Each of these esters, on solvolysis, should give rise to a carbonium ion (A↔B) stabilized by essentially the same electronic features which stabilize the corresponding cyclocholesteryl cations.[2]



Results and Discussion

The kinetic data are summarized in Table I. Each of the esters was allowed to solvolyze in 60 volume per cent. aqueous acetone and the course of reaction was followed by titrating the liberated *p*-nitrobenzoic acid. The reactions followed strictly the first-order kinetic law, and furnished, within experimental error, 100% of the theoretical acid. Thus, little or no rearrangement to less reactive isomeric esters accompanies solvolysis in this solvent system.

That the hydrolysis of these esters takes place *via* an uncatalyzed, alkyl–oxygen fission reaction is evidenced by the strict adherence of the rates to first-order kinetics, the sensitivity of the reaction rate to *p*-methyl substitution, and the magnitude of the reaction rates (*vide infra*).

(2) The experiments described in this communication complement the recently reported results of Hart and Sandri.[3] These authors measured the rates of solvolysis in aqueous dioxane of a series of tertiary carbinyl *p*-nitrobenzoates substituted with isopropyl and cyclopropyl groups. They found that "as isopropyl groups were successively replaced by cyclopropyl, the rate increased, with the second cyclopropyl group causing a rate enhancement nearly equal to that of the first." The products of solvolysis of these esters were shown to be unrearranged and the authors conclude that "rates, products and energetics can be interpreted in terms of a . . . mechanism which includes stabilizing the positive charge in the carbonium ion by *each* cyclopropyl group."

(3) H. Hart and J. M. Sandri, THIS JOURNAL, **81**, 320 (1959).

TABLE I

RATES OF SOLVOLYSIS OF SOME SECONDARY CYCLOPROPYL *p*-NITROBENZOATES IN 60 VOLUME PER CENT. AQUEOUS ACETONE

Cyclopropylcarbinyl *p*-nitrobenzoate	Temp., °C.	k, sec.$^{-1}$ × 10^5
Methyl[a]	65	0.254 ± 0.005
	75	0.582 ± .009
	85	1.64 ± .02
Phenyl[b]	25	0.524 ± .008
	35	1.75 ± .01
	50	10.0 ± .2
	65[d]	47.4[d]
p-Tolyl[c]	25	5.20 ± 0.01
	35	18.7 ± 0.3
	65[d]	565[d]

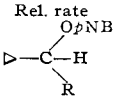
[a] $\Delta H^*(65\text{–}85)$ = 21.3 kcal./mole, $\Delta S^*(65)$ = −21.2 e.u.; these thermodynamic functions were not constant with temperature. [b] ΔH^* = 21.9 kcal./mole, ΔS^* = −8.9 e.u. [c] ΔH^* = 22.9 kcal./mole, ΔS^* = −1.6 e.u. [d] Extrapolated.

The only non-acidic product of the solvolysis of phenylcyclopropylcarbinyl *p*-nitrobenzoate, under kinetic conditions, proved to be the unrearranged parent alcohol, phenylcyclopropylcarbinol, as was shown by vapor phase chromatography of the solvolysis mixture (after extraction of acidic components). The spectrum contained only a single peak (after elution of solvent) whose retention time proved to be identical with that of authentic phenylcyclopropylcarbinol. Ultraviolet spectroscopy confirmed the absence of appreciable amounts of one possible rearrangement product, γ-phenylallylcarbinol.

Table II compares the relative rates of solvolysis of methyl-, phenyl- and *p*-tolylcyclopropylcarbinyl *p*-nitrobenzoate in 60 volume per cent. aqueous acetone at 65° with the relative rates of solvolysis of correspondingly substituted cholesteryl *p*-toluenesulfonates[1b,c] in 90 volume per cent. aqueous dioxane at 50°.

TABLE II

COMPARISON OF RELATIVE RATES OF SOLVOLYSIS OF SOME CYCLOPROPYLCARBINYL *p*-NITROBENZOATES AND OF SOME CHOLESTERYL *p*-TOLUENESULFONATES

R	Rel. rate 6-R-cholesteryl OTs	Rel. rate 
Methyl	1.00	1.00
Phenyl	0.00426	179
p-Tolyl	0.00615	2140

It can be seen that, in the solvolysis of the cyclopropylcarbinyl esters, the stabilizing abilities of alkyl and aryl groups are in marked contrast to their effectiveness in the solvolyses of cholesteryl esters. As in shown below the order of reactivity displayed by the cyclopropyl series parallels quite closely the orders of reactivity accompanying similar changes in structure in other systems.

That the unusual reactivity order observed with the cholesteryl esters does not have its origin in the conjugation energy of the styrene systems of the arylcholesteryl esters is shown by the effectiveness

of *p*-methyl substitution into the phenyl ring of phenylcyclopropyl *p*-nitrobenzoate; a rate increase of 10.7 accompanies this structural change, whereas a corresponding factor of only 1.44 was observed when a similar change was made in 6-phenylcholesteryl *p*-toluenesulfonate. We have recently shown[4] that substitution of a *p*-methyl group into the phenyl rings of α-phenyl-γ-methylallyl and α-methyl-γ-phenylallyl *p*-nitrobenzoate results in solvolysis rate enhancements of 10.4 and 8.6, respectively (60 volume per cent. aqueous dioxane, 25°), in spite of the fact that the conjugated γ-aryl esters have been shown by kinetic methods to be *ca.* 3.2 kcal./mole more stable than their corresponding α-aryl esters.[5] Thus, in this allylic system, the sensitivity of reaction rates to *p*-methyl substitution is *nearly independent of ground state energy.* Accordingly, it is concluded that the relatively low sensitivity to *p*-methyl substitution of 6-phenylcholesteryl *p*-toluenesulfonate must result from factors other than ground state energy differences.

The present work also makes it probable that the ineffectiveness of aryl groups in promoting the ionization of cholesteryl esters is not due to stereoelectronic factors. For if it were a similar sensitivity to aryl substitution should have been observed in both the cyclopropylcarbinyl and cholesteryl series (after correction for ground state energy differences). In actual fact the effects of substitution in the cyclopropylcarbinyl series parallel very closely the effects of similar structural changes in other systems, leading to the conclusion that both the cyclopropyl and aryl rings exert their stabilizing effects on a positive carbon atom in an independent, cumulative fashion. Thus the factor of 10.6 in rate accompanying *p*-methyl substitution in phenylcyclopropyl carbinyl *p*-nitrobenzoate at 25° compares with the very similar factors, 8.6–10.4, accompanying this same substitution into phenylallyl systems[4] and an average factor of *ca.* 20 accompanying *p*-methyl substitution into many benzylic systems undergoing solvolysis reactions under similar conditions.[6a] Further, the rate enhancement accompanying the replacement of the methyl group in methylcyclopropylcarbinyl *p*-nitrobenzoate by phenyl, a factor of 179, compares with effects associated with similar structural changes in other systems. Thus the relative rates of solvolysis of *t*-butyl chloride and cumyl chloride in 90 volume per cent. aqueous acetone at 25° are 1:620[6b] and the relative rates of solvolysis of α-phenylethyl chloride and benzhydryl chloride in 80 volume per cent. aqueous acetone are 1:143.[6b]

A portion of the discrepancy between the ratio of solvolysis rates of typical α-phenyl and α-methyl substituted compounds, $k_{\alpha\text{-phenyl}}/k_{\alpha\text{-methyl}} \cong 200$, and the corresponding ratio in the cholesteryl series, $k_{\delta\text{-phenyl}}/k_{\delta\text{-methyl}} = 0.00426$, is accounted for by the extra ground state resonance stabilization of the conjugated 6-phenylcholesteryl *p*-toluenesulfonate. Depending on the degree of planarity of the styrene system in the ground state of this molecule, this conjugation energy may be as high as 3.2 kcal./mole,[4] corresponding to a rate factor of 118 at 65°. However, even after account is taken of this factor, the phenyl group of 6-phenyl-cholesteryl *p*-toluenesulfonate is still found to be less effective than is a 6-methyl substituent in stabilizing the transition state ($0.00426 \times 118 = 0.50$).

If the substituted cyclopropylcarbinyl esters studied in this work are reasonable electronic models for the corresponding cholesteryl systems, our results clearly indicate that the anomalous reactivity order observed with the cholesteryl series is not a result of either ground state stabilization or stereoelectronic phenomena, and point to a third factor, steric inhibition of resonance, as the source of the unusual results.[7]

Experimental

Preparation of Rate Solutions.—Acetone was distilled successively from potassium permanganate, potassium carbonate and Drierite. Three volumes of this acetone were added to two volumes of deionized, carbonate-free water (prepared by passing distilled water through a series of ion-exchange columns, the last of which was packed with Amberlite MB-3 cation–anion exchange resin), thus making 60 volume per cent. aqueous acetone. This solution was added to a weighed amount of the *p*-nitrobenzoate ester under study. For runs at temperatures above 50° it was convenient to use ampoules. Approximately 7–8 ml. of the acetone–water solution of the ester was introduced into each glass ampoule and sealed under nitrogen. At temperatures below 50° the reactions were run in 100-ml. volumetric flasks.

Kinetic Measurements.—Aliquots were quenched in 10 ml. of acetone and titrated to the phenolphthalein end-point with *ca.* 1.7×10^{-2} *M* potassium hydroxide. Infinity titers were measured after *ca.* 10 half-lives. In many cases infinity titers were also measured after 20 or more half-lives, and were found to be essentially unchanged. In general, the rate constants reported in Table I were calculated from 8–13 experimental points. A typical kinetic run is illustrated in Table III.

TABLE III

SOLVOLYSIS OF 8.80×10^{-3} *M* *p*-TOLYLCYCLOPROPYLCARBINYL *p*-NITROBENZOATE IN 60 VOLUME PER CENT. AQUEOUS ACETONE AT 35.0°

[KOH] = 1.748×10^{-2} *M*; theoretical infinity titer = 2.536 ml.; % theory = 2.570/2.536 = 101.3%

Time, sec. $\times 10^{-3}$	KOH, ml.	k, sec.$^{-1}$ $\times 10^4$	Time, sec. $\times 10^{-3}$	KOH, ml.	k, sec.$^{-1}$ $\times 10^4$
0.000	0.410	..	3.780	1.460	1.80
0.540	.620	1.88	4.800	1.640	1.80
1.020	.790	1.94	7.500	2.000	1.84
1.440	.910	1.87	8.340	2.072	1.83
1.860	1.020	1.81	9.600	2.210	1.95
2.400	1.150	1.77	12.42	2.300	..
2.880	1.265	1.78	∞	2.570	..
3.300	1.370	1.82		Av.	1.84 ± 0.05

Methylcyclopropylcarbinol.—To a 500-ml. three-necked flask equipped with mechanical stirrer, vapor by-pass dropping funnel and drying tube was added 150 ml. of a

(4) R. A. Sneen, THIS JOURNAL, **82**, 4261 (1960).

(5) These facts, incidentally, justify the assumption that the sensitivity of both the cholesteryl and cyclopropylcarbinyl systems to substitution should be electronically similar in spite of the fact that the starting esters of the two series are homoallylically related.

(6) (a) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 648 (1956); (b) **56**, 616 (1956); (c) **56**, 668 (1956).

(7) Winstein and Kosower[8] have recently pointed out that an essential difference may exist between the bonding in ions derived from cyclopropylcarbinyl systems and in cyclocholesteryl cations, since the latter are constrained by the rigid fused ring system in such a manner as to prevent any important resonance interaction between C_8 and the geometrically inaccessible C_6 of the cholesteryl nucleus. Although the extent of the differences in resonance stabilization of cholesteryl and cyclopropylcarbinyl systems is not clear, we feel it probable that the stereoelectronic requirements of both the homoallylic and cyclopropylcarbinyl-derived ions should be similar.

(8) S. Winstein and E. M. Kosower, THIS JOURNAL, **81**, 4399 (1959).

1.0 *M* lithium aluminum hydride solution in absolute ether. Methyl cyclopropyl ketone (Columbia redistilled, b.p. 121–121.5°, $n^{21}D$ 1.4310, 24.1 g.), dissolved in 200 ml. of absolute ether, was added dropwise with stirring. Stirring at room temperature was continued for 24 hours after the addition of the ketone was complete. Saturated, aqueous sodium potassium tartrate (*ca.* 100 ml.) was added dropwise to the cooled (0°) reaction mixture. The phases were separated, the aqueous phase extracted with ether and the ethereal extract added to the organic layer. The solution was dried over anhydrous sodium sulfate, concentrated to remove most of the ether, and distilled through a small column packed with glass beads. Methylcyclopropylcarbinol was obtained in 68.5% yield (b.p. 121–121.5°, $n^{21}D$ 1.4310).

Phenyl Cyclopropyl Ketone.—The phenyl Grignard reagent was prepared according to the prodedure of Fieser.[9] To a 200-ml. three-necked flask containing 0.20 mole of freshly prepared phenyl Grignard reagent was added cyclopropyl cyanide (Matheson, Coleman and Bell, used as supplied, 11 g.), in ether, dropwise. After the addition was complete the reaction mixture was stirred for 1 hour at room temperature and then cooled to *ca.* 0°. Hydrochloric acid (8%, 1300 ml.) was added, slowly at first and then more rapidly. The mixture was warmed to room temperature and stirred for 15 hours. The phases were separated, and the aqueous layer was extracted with ether. The extract was added to the organic layer and treated with sodium carbonate. The organic layer was then filtered twice through anhydrous sodium sulfate to remove traces of water. The filtrate was distilled through a Vigreux column to remove most of the ether, and the residue was distilled through a small column packed with glass beads. Phenyl cyclopropyl ketone was obtained in 69% yield (16.2 g., b.p. 103–104° (3 mm.), $n^{25}D$ 1.5541). Henze and Gayler[10] report b.p. 125° (20 mm.), $n^{20}D$ 1.5525, while Close[11] reports b.p. 109–110° (10 mm.), $n^{25}D$ 1.5515.

Phenylcyclopropylcarbinol.—The procedure described above for the preparation of methylcyclopropylcarbinol was followed. From cyclopropyl phenyl ketone (15 g.) was obtained in 90% yield the carbinol, 13.6 g., b.p. 87–88° (1 mm.), $n^{12}D$ 1.5451. Close[10] reports b.p. 121°(12 mm.), $n^{25}D$ 1.5390.

***p*-Tolyl Cyclopropyl Ketone.**—The procedure described above for the preparation of phenyl cyclopropyl ketone was followed, using *p*-bromotoluene (b.p. 84°(25 mm.), 35 g.), magnesium turnings (5.00 g.) and cyclopropyl cyanide (10.9 g.). The ketone was obtained in 38.5% yield (10.0 g., m.p. *ca.* 35°), and was reduced to the corresponding alcohol without further purification.

***p*-Tolylcyclopropylcarbinol.**—The procedure described above for the preparation of methylcyclopropylcarbinol was followed. From 10.0 g. of *p*-tolylcyclopropyl ketone was obtained 6.47 g. (64% yield) of the carbinol, b.p. 118–122°(11 mm.), $n^{25}D$ 1.5375.

Anal. Calcd. for $C_{11}H_{14}O$: C, 82.05; H, 8.70. Found: C, 82.23; H, 8.69.

Phenylcyclopropylcarbinyl *p*-Nitrobenzoate.—To a magnetically stirred mixture of phenylcyclopropylcarbinol (3.950 g.) and pyridine (30 ml., distilled from calcium hydride), in a 50-ml. erlenmeyer flask at 0°, was added *p*-nitrobenzoyl chloride (3.58 g., recrystallized from benzene–pentane) portionwise. After the addition of the acid chloride was complete, stirring was continued at room temperature for 1 hour. The mixture was then poured into a beaker containing ice and water. The precipitated crystals were collected by filtration and immediately recrystallized from *ca.* 60% aqueous acetone. The *p*-nitrobenzoate ester of phenylcyclopropylcarbinol was obtained in 73.5% yield (2.91 g., m.p. 159–162°).

Anal. Calcd. for $C_{17}H_{15}O_4N$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.55; H, 5.12; N, 4.70.

Methylcyclopropylcarbinyl *p*-Nitrobenzoate.—The procedure described above for the preparation of the *p*-nitrobenzoate of phenylcyclopropylcarbinol was followed. From methylcyclopropylcarbinol (0.648 g.), *p*-nitrobenzoyl chloride (1.040 g.) and pyridine (15 ml.) was obtained the ester in 53.5% yield (0.700 g., m.p. 63.2–63.8°).

Anal. Calcd. for $C_{12}H_{13}O_4N$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.33; H, 5.65; N, 6.29.

***p*-Tolycyclopropylcarbinyl *p*-Nitrobenzoate.**—The procedure described above for the preparation of the *p*-nitrobenzoate of phenylcyclopropylcarbinol was followed. From *p*-tolylcyclopropylcarbinol (0.920 g.), *p*-nitrobenzoyl chloride (1.05 g.) and pyridine (15 ml.) was obtained the ester in 26.6% yield (0.460 g., m.p. 69–70°).

Anal. Calcd. for $C_{18}H_{17}O_4N$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.66; H, 5.73; N, 4.66.

Product Studies. A. Vapor Phase Chromatography.—Phenylcyclopropylcarbinyl *p*-nitrobenzoate (299 mg.) was solvolyzed in 100 ml. of 60 volume per cent. aqueous acetone at 35° for 10 half-lives. The reaction mixture was extracted exhaustively with ether, the ethereal layer was dried (sodium sulfate) and most of the ether was removed by distillation. Injection of a sample of this solution into vapor fractometer (silicone oil, 176°) gave, almost immediately, a strong peak corresponding to volatile solvent. The only other absorption was a strong, sharp peak with retention time 1.5 minutes. A sample of authentic phenylcyclopropylcarbinol in acetone gave an identical chromatogram, with the same retention time.

B. Ultraviolet Spectrophotometry.—The solvolysis of 0.234 g. of phenylcyclopropylcarbinyl *p*-nitrobenzoate in 100 ml. of 60% aqueous acetone was carried out for 36 half-lives of reaction at 35°. A 5-ml. aliquot of the reaction mixture was shaken with 5 ml. of 0.04 *N* alcoholic potassium hydroxide, 25 ml. of water was added and the mixture was extracted four times with 10-ml. portions of ether. The resulting ethereal solution was extracted five times with 10-ml. portions of 0.04 *N* potassium hydroxide, and was then diluted to 1000 ml. with ether. Ultraviolet analysis on a Cary spectrophotometer, model 14, using a 1-cm. cell, indicated negligible absorbance in the 240–250 mμ region.[12]

Acknowledgment.—This investigation was supported by a research grant, RG-6297, from the National Institutes of Health, Public Health Service, whose assistance is gratefully acknowledged.

(9) L. F. Fieser, "Experiments in Organic Chemistry," third edition, D. C. Heath and Co., Boston, Mass., 1955, p. 79.

(10) H. R. Henze and C. W. Gayler, THIS JOURNAL, **74**, 3615 (1952).

(11) W. J. Close, *ibid.*, **79**, 1456 (1957).

(12) Styrene[13] has λ_{max} 245 mμ, log ε 4.15.

(13) A. C. Cope and M. Burg, THIS JOURNAL, **74**, 168 (1952).