

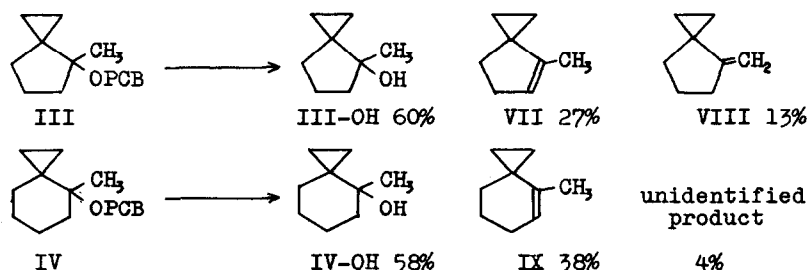
STRUCTURE AND REACTIVITY OF SMALL RING COMPOUNDS II. SOLVOLYSIS
STUDIES ON SOME CYCLOPROPYLCARBINYL-TYPE DERIVATIVES OF SPIRANS

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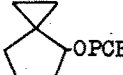
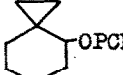

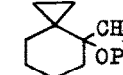
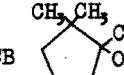
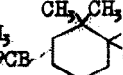
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The kinetic studies on the solvolysis of 4-methyl spiro[2,4]heptan-4-yl and 4-methyl spiro[2,5]octan-4-yl *p*-chlorobenzoates, and their corresponding secondary derivatives were carried out in an aqueous solution of dioxane. The kinetic results are shown in Table I. The solvolysis of tertiary spiro esters gave following products and no rearranged product was obtained.



The vpc analysis of the solvolysis product of III indicated the presence of only three components (13:27:60). The latest component was identified as III-OH by the comparison with the infrared and nmr spectra of the authentic sample. The structures of the residual two components were confirmed from the spectral data. The nmr spectrum of the second component showed a presence of olefinic proton at 4.73 τ (multiplet, area 1), allylic protons at ca. 7.65 τ (complex multiplet, area 2), methyl protons at 8.65 τ (doublet $J=2$ c.p.s., area 3) and homoallylic protons (three partially resolved multiplets at 8.04, 8.11 and

Table I. Solvolysis Results of *p*-Chlorobenzoates
in aqueous Dioxane at 100.45°

Ester							
	I	II	III	IV	V	VI	
$k, \times 10^3$ in 85% dioxane (sec^{-1})			25.8 ^{a)}	2.01 ^{b)}			
$k, \times 10^5$ in 60% dioxane (sec^{-1})	6.18	1.58	15.7×10^4 ^{c)}	1.22×10^4 ^{c)}	8.92	0.539	
relative rate in 85% dioxane			13	1.0			
relative rate in 60% dioxane	3.9	1.0	—	7,700			
		1.0	—	26,000			
				18,000	—	1.0	
					23,000	17	1.0

a) Calculated for 100.45° from the measurements at 25, 40 and 55°. b) Calculated for 100.45° from the solvolysis rates at 50, 65 and 80°. c) The rate in 60% dioxane was obtained using the ratio of (k_W in 60% dioxane/ k_W in 85% dioxane) at 45°, which was 60.8.

8.17 τ , total area 2). Two multiplets appeared at ca. 9.35 and 9.55 τ (total area 4) showed symmetrical A_2B_2 spectrum and these multiplets were assigned to cyclopropane protons.⁽¹⁾ The infrared spectrum showed the bands expected for a cyclopropyl group (3055 and 1017 cm^{-1}), a methyl group (1380 cm^{-1}) and a tri-substituted olefin (1646 and 808 cm^{-1}).⁽²⁾ On the basis of these data the second component was identified as 4-methyl spiro[2,4]hept-4-ene VII.

The first component was identified similarly as 4-methylene spiro[2,4]-heptane VIII from its spectra. In the nmr spectrum, two olefinic protons appeared at 5.51 and 5.83 τ as two triplets (both $J=2$ c.p.s.), two allylic protons at ca. 7.55 τ as a complex multiplet and four cyclopropane protons at 9.30 τ as a multiplet. The infrared spectrum also showed a presence of a cyclopropyl group (3060 and 1011 cm^{-1}) and an *exo*-cyclic methylene group (1650 cm^{-1}).

The vpc analysis of the solvolysis product of IV showed the presence of

three components (4:38:58). The latest component was identified as IV-OH by the comparison with the infrared and nmr spectra of the authentic sample. The structure of the second component was confirmed from its spectra. The nmr spectrum of the second component showed a presence of olefinic proton at 4.65 τ (multiplet, area 1), allylic protons at 7.98 τ (complex multiplet, area 2) and methyl protons at 8.67 τ (doublet $J=2$ c.p.s., area 3) together with residual four cyclohexyl protons from 8.2 to 8.8 τ . Two complex multiplets appeared at ca. 9.28 and 9.71 τ were assigned to four cyclopropane protons.⁽¹⁾ The infrared spectrum contained bands expected for a cyclopropyl group (3065 and 1012 cm^{-1}), a methyl group (1377 cm^{-1}) and a trisubstituted olefin (1655 and 808 cm^{-1}).⁽²⁾ From these results, the second component was identified as 4-methyl spiro[2,5]-oct-4-ene IX.

Spiro esters III and IV solvolyze faster than the corresponding 1,2,2-trimethyl derivatives V and VI by a factor of 2×10^4 as shown in Table I. Nevertheless the structures of all solvolysis products of these esters were found to keep those of starting materials and no rearranged product was obtained.

It has been proposed that the high reactivity of cyclopropylcarbinyl derivatives is due to the resonance between cyclopropane ring and the electron deficient center such as non-classical or hyperconjugative resonance.⁽⁴⁾⁽⁵⁾ The both intermediates should give rearranged products, since the product distribution will be a qualitative reflection of charge distribution in the intermediate.⁽⁶⁾ The results obtained suggest that the positive charge in the intermediate localizes mostly at the reaction center and, accordingly, the intermediate is essentially classical in spite of the observed large rate enhancement.

The localization of charge at the reaction center in the transition state is also supported by the following fact. It has been shown that a methyl substituent at the reaction center increases a rate of solvolysis of cyclopentyl and cyclohexyl derivatives by factors of 175,000 and 33,000 respectively. In spiro esters I and II, substitution of hydrogen by methyl group was found similarly to increase a rate of solvolysis by factors of 26,000 and 7,700 as shown in Table I. However, the effect of rate enhancement is far smaller in resonance-stabilized systems⁽⁷⁾ : 1-phenyl ethyl, 1,800; benzhydryl, 346.

If cyclopropylcarbinyl system is a resonance-stabilized system, the effect of methyl substituent on rate enhancement should be much smaller than the effect in alicyclic system and similar to that in the resonance-stabilized system. The above results of relative rate suggest that the spiro cyclopropylcarbinyl system is similar to the alicyclic system rather than the resonance-stabilized system.

Thus it seems to be difficult to interpret the high reactivity of cyclopropylcarbinyl derivatives in terms of the resonance alone between cyclopropane ring and the electron deficient center. Then it is necessary to consider the contribution of another factor to recognize the peculiarity of this system. Other spiro compounds are currently under investigation to clarify the effect of cyclopropyl group and the results will be reported in the near future.

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