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Structure and Reactivity of Small Ring Compounds. III. Solvolyses of 4-Methyl Spiro[2, 4]hept-4-yl and 4-Methyl Spiro[2, 5]oct-4-yl *p*-Chlorobenzoates

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The solvolyses of 4-methyl spiro[2, 4]hept-4-yl, 4-methyl spiro[2, 5]oct-4-yl, 1, 2, 2-trimethylcyclopentyl, 1, 2, 2-trimethylcyclohexyl, spiro[2, 4]hept-4-yl, and spiro[2, 5]oct-4-yl *p*-chlorobenzoates have been examined in an aqueous solution of dioxane. The rate of the solvolysis of 4-methyl spiro[2, 4]hept-4-yl *p*-chlorobenzoate was 26000 times greater than that of the corresponding secondary derivatives and 18000 times greater than that of the 1, 2, 2-trimethylcyclopentyl derivative. Similarly, in the cyclohexyl series, 4-methyl spiro[2, 5]-oct-4-yl *p*-chlorobenzoate solvolyzed 7700 times faster than the sprio[2, 5]oct-4-yl ester and 23000 times faster than the 1, 2, 2-trimethylcyclohexyl ester. All the solvolysis products of tertiary spiro derivatives kept the skeletons of the starting materials entirely. Thus, the 4-methyl spiro[2, 4]hept-4-yl ester gave a mixture of 4-methyl spiro[2, 4]hept-4-ol (60%), 4-methyl spiro[2, 4]hept-4-ene (27%), and 4-methylene spiro[2, 4]heptane (13%). The 4-methyl spiro[2, 5]oct-4-yl ester gave the original alcohol (58%) and 4-methyl spiro[2, 5]oct-4-ene (38%), along with a small amount of an unidentified product. The implications of these results are discussed.

Although the unusual high reactivity of cyclopropylcarbinyl derivatives observed in the unimolecular solvolytic reaction has been the subject of much research and debate,[1-13] no clear interpretation of this matter has been presented. In a previous paper,[14] the solvolytic reactivities and reaction products of secondary spiro cyclopropylcarbinyl derivatives have been studied, and the contradictions in the some interpretations proposed in the past pointed out.

In the present study, the solvolyses of tertiary spiro cyclopropylcarbinyl derivatives, I and II, have been investigated, and the mechanism of high reactivity observed in the cyclopropylcarbinyl derivatives discussed. The study of the solvolysis of these compounds is interesting for the following reasons. It can be expected that the more the charge in the intermediate is delocalized, the less is the rate enhancement due to a methyl substituent at the reaction center. Actually, the rate enhancement by replacing a hydrogen with a methyl substituent at the reaction center is much smaller in resonance-stabilized systems such as those of benzyl derivatives.[15] The high reactivity of cyclopropylcarbinyl derivatives in a unimolecular solvolytic reaction was attributed to a non-classical intermediate, the bicyclobutonium ion, by Roberts,

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2) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

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9) K. B. Wiberg and A. J. Ashe III, *Tetrahedron Letters*, **1965**, 1553, 4245; K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. S. Schertler and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

10) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London (1962); H. C. Brown and J. D. Cleveland, *J. Am. Chem. Soc.*, **88**, 2051 (1966).

11) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965).

12) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965); N. C. Deno, H. G. Richey, Jr., J. S. Kiu, D. N. Lincoln and J. O. Turner, *ibid.*, **87**, 4533 (1965).

13) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966).

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15) H. C. Brown and M. H. Rei, *J. Am. Chem. Soc.*, **86**, 5008 (1964).

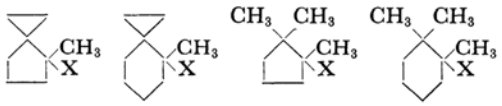
and, according to Roberts, the non-classical formulation involves a delocalization of the charge.[1] Thus the effect of the methyl substituent in the cyclopropylcarbinyl system should be smaller than that in acyclic and alicyclic systems if the high reactivity of those derivatives is purely due to a non-classical resonance stabilization of the intermediate.

Winstein and Grunwald[16] have pointed out that, as substitution about the reacting center is increased, participation becomes less important as a means of distributing the positive charge. Therefore, supposing that the effect of the cyclopropyl group results from the participation of this function, the effect of a cyclopropyl substituent on the reactivity in a tertiary cyclopropylcarbinyl derivative should be less than that in a secondary derivative.

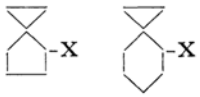
The present study includes the solvolyses of 4-methyl spiro[2,4]hept-4-yl, 4-methyl spiro[2,5]oct-4-yl, 1, 2, 2-trimethylcyclopentyl, 1, 2, 2-trimethylcyclohexyl, spiro[2,4]heptan-4-yl, and spiro[2,5]oct-4-yl *p*-chlorobenzoates; their solvolytic reactivities and reaction products will be examined.

Results

Compounds and Kinetics. The kinetic measurement were carried out on the following esters:



Ia, b IIa, b IIIa, b IVa, b



Va, b VIa, b

a) X=-OH, b) X=-OCO-  -Cl (-OPCB)

These esters were successfully prepared following the procedure of Hart and Law.[4] The solvolysis rates in an aqueous solution of dioxane were measured by titrating the liberated *p*-chlorobenzoic acid potentiometrically with alkali, as has been described in a previous paper.[14] The ester studied must have solvolyzed with unimolecular alkyl-oxygen fission. This conclusion is supported by the following evidence.[17] The kinetic were clearly first-order throughout the reaction. The methanolysis of Ib and IIIb gave *p*-chlorobenzoic acid quantitatively, and no alcohol was detected in the products, by vpc analysis. The solvolysis rate of IIb was increased greatly by increasing the ionizing power of the solvent. The kinetic results are summarized in Table 1, while the relative rates are shown in Table 2.

Solvolysis Products. All the solvolysis products of Ib and IIb kept the carbon skeletons of the starting materials entirely, and no rearranged product was obtained. The solvolysis of Ib gave alcohol and olefin in 60% and 40% yield respectively. The alcohol product consisted of only one component, as determined by vpc analysis; this was identified as the original alcohol, Ia, by the identity of their spectra. The olefin product was composed of two components (68 : 32); their structures were confirmed by elemental analysis and by a study of a spectral data.[18,19] In the NMR spectrum of the major component, an olefin proton appeared as a multiplet at 4.73 τ; two allyl protons, as a complex multiplet at *ca.* 7.65 τ; two homoallyl protons, as a partially-resolved multiplets at 8.04, 8.11, and 8.17 τ, and three methyl protons, as a doublet (J=2 cps) at 8.65 τ. Two cyclopropane protons *syn* to the double bond appeared at *ca.* 9.35 τ and two *anti* cyclopropane protons, at *ca.* 9.55 τ, in a typical A_2B_2 pattern. The IR spectrum showed absorption at 3055, 1646, 1380, and 1017 cm^{-1}; these absorptions were assigned to the cyclopropane C–H steretch, C=C stretch, the methyl C–H deformation, and the skeletal vibration of the cyclopropane ring respectively. On the basis of these results and of the elemental analysis, the major component was identified as 4-methyl spiro[2, 4]hept-4-ene.

The minor component was similarly identified as 4-methylene spiro[2, 4]heptane on the basis of its spectra and the results of elemental analysis. The NMR spectrum showed two triplets (both J=2 cps) at 5.51 and 5.83 τ (area 2), which were assigned to *anti* and *syn* olefin protons to the cyclopropane ring. It showed, in addition, a complex multiplet at *ca.* 7.55 τ (area 2) which was assigned to allyl protons; two partially-resolved multiplets at 8.76 and 8.79 τ (area 4) which were assigned to residual cyclopentane protons, and a multiplet at 9.30 τ (area 4) which was assigned to cyclopropane protons. The IR spectrum contained bands expected for a cyclopropyl group (3060, 1011 cm^{-1}) and an exo-cyclic methylene group (1650 cm^{-1}).

The solvolysis of IIb gave alcohol and olefin in 58% and 38% yields respectively, along with a small amount of an unidentified product (4%). Both the alcohol and olefin consisted of one components, as was shown by vpc analysis; the alcohol was identified as Ia through the comparison of its

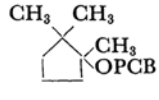
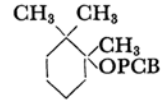
16) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).
17) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y. (1953).
18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Willy and Sons, Inc., N. Y. (1958).
19) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York (1959).

Table 1. Solvolysis results

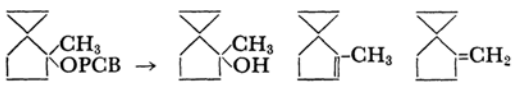
Ester	Aq. dioxane wt%	Temp., °C[a]	$k_1 \times 10^5$, sec^{-1}	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e. u.
Ib	85	25.40	1.68±0.02	21.1	− 9.8
		40.20	8.98±0.03		
		55.32	43.3±0.3		
IIb	85	49.69	1.23±0.02	23.3	− 9.1
		64.70	6.75±0.08		
		79.98	31.0±0.6		
	60	45.39	46.4±0.4		
IIIb	60	85.19	2.27±0.06	25.0	−10.6
		100.00	8.55±0.12		
		116.13	39.6±1.4		
IVb	60	100.07	0.521±0.003		
Vb	60	100.45	6.18±0.12		
VIb	60	100.45	1.58±0.03		

a) Temperature deviation of ±0.02°C.

Table 2. Relative solvolysis rates of *p*-chlorobenzoates in aqueous dioxane at 100.45°C

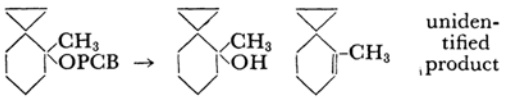
Compound	 Ib	 IIb	 IIIb	 IVb	 Vb	 VIb
$k_1 \times 10^3$ in 85% dioxane (sec^{-1})	25.8[a]	2.01[b]				
$k_1 \times 10^5$ in 60% dioxane (sec^{-1})	15.7×10^4 [c]	1.22×10^4 [c]	8.92	0.539[d]	6.18	1.58
Relative rate in 85% dioxane	13	1.0				
Relative rate in 60% dioxane	18000	23000	17	1.0		
		—	1.0			
	26000	7700	—	—	3.9	1.0
		—	—	—	1.0	

a) Calculated for 100.45°C from the measurements at 25, 40 and 55°C. b) Calculated for 100.45°C from the rates at 50, 65 and 80°C. c) The rate in 60% dioxane was obtained using the ratio of (k_{IIb} in 60% dioxane/k_{IIb} in 85% dioxane) at 45.39°C, which was 60.8. d) Calculated for 100.45°C using the ratio of (k_{Vb} at 100.45°C/k_{Vb} at 100.07°C), which was 1.03.



Ib Ia 60% VII 27% VIII 13%

Fig. 1



IIb IIa 58% IX 38% 4%

Fig. 2

spectra with those of an authentic sample. In the NMR spectrum of the olefin component, an olefin proton appeared at 4.65 τ as a multiplet; two allyl protons, at *ca.* 7.98 τ as a complex multiplet; four residual cyclohexane protons, from 8.2 τ to 8.8 τ as a complex multiplet, and three methyl protons, at 8.67 τ as a sharp doublet (J= 2 cps). Four cyclopropane protons appeared at 9.82 τ and 9.71 τ as multiplets which were assigned to the *syn* and *anti* protons to the double bond respectively. The IR spectrum contained bands expected for a cyclopropyl group (3065, 1012 cm^{-1}) and an olefinic bond (1655 cm^{-1}). From these spectral data and the results of elemental analysis, the olefin was identified as 4-methyl spiro-[2, 5]oct-4-ene. The results of the product analyses are shown in Figs. 1 and 2.

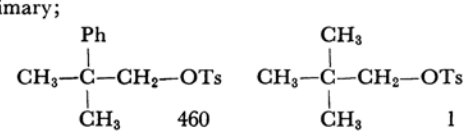
Discussion

It has been well known that there are various neighboring nucleophilic functions which

accelerate the nucleophilic substitution reaction.[20] This effect has been interpreted in terms of participation by a neighboring group. The cyclopropane ring has a nucleophilic character,[21] and, accordingly, the participation of a cyclopropyl group may be inferred as a factor providing the high reactivity of cyclopropylcarbinyl derivatives. Winstein and Grunwald[16] have pointed out that, as substitution about the reacting center is increased, participation becomes less important as a means of distributing the positive charge. Thus, the more the substitution at the reaction center is increased, the less is the rate enhancement due to neighboring group participation. For example, the rate enhancement due to the phenyl group at the β-position decreases rapidly as the substitution at the reaction center is increased and becomes negligible in the tertiary carbinyl derivative, as is shown in Table 3.

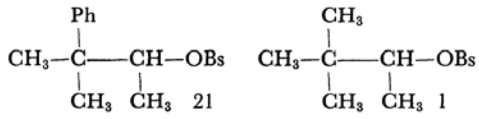
TABLE 3

Primary;



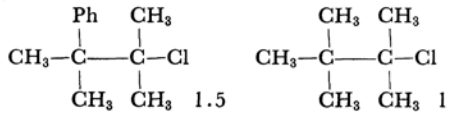
in AcOH at 50°C[22]

Secondary;



in AcOH at 50°C[22]

Tertiary;



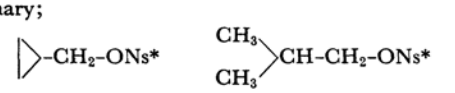
in 80% EtOH at 25°C[23]

On the contrary, a cyclopropyl group accelerates the solvolysis rate of cyclopropylcarbinyl derivatives by a factor of 10^4—10^6, without distinction of the degree of substitution at the reaction center, as Table 4 shows. This result suggests that the unusual reactivity of cyclopropylcarbinyl derivatives does not result from the participation of the cyclopropane ring.

It has been known that rate enhancement by a methyl substituent at the reaction center is far smaller in a resonance-stabilized system than in acyclic and alicyclic systems.

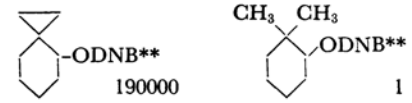
TABLE 4

Primary;



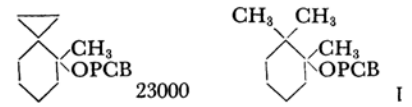
in AcOH at 25°C[24]

Secondary;



in 60 wt% aq. dioxane[14] at 100°C

Tertiary;



in 60 wt% aq. dioxane at 100°C

* β-naphthalenesulfonate
** 3,5-dinitrobenzoate

A methyl substituent, for example, increases the limiting rate of the solvolysis of cyclopentyl and cyclohexyl derivatives by factors of 175000 and 33000 respectively.[15] On the other hand, the effect is much smaller in a resonance-stabilized system; 1-phenylethyl, 1800; benzhydryl, 346. Thus, if cyclopropylcarbinyl derivatives solvolyze through the resonance-stabilized intermediate, the effect of a methyl substituent in those systems should be much smaller than its effects in acyclic and alicyclic systems. Moreover, since the cyclopropyl group stabilizes a neighboring electron-deficient center much more than a vinyl or phenyl group does,[1-5,10-14] the effect of a methyl substituent in a cyclopropylcarbinyl system should be smaller compared even with the effect in a phenylethyl system. However, the observed effects on spiro-[2, 4]heptyl and spiro[2, 5]octyl derivatives exceed that in the 1-phenylethyl derivative and are nearly those observed on the corresponding alicyclic derivatives. Therefore, it seems to be difficult to interpret the high reactivity of cyclopropylcarbinyl derivatives in terms of an intermediate stabilized by non-classical resonance[1] or hyperconjugative resonance.[3,4]

The spiro esters Ib and IIb kept their carbon skeletons intact throughout the solvolytic reaction. Nevertheless, the cyclopropane ring accelerates

20) A. Streitwieser, Jr., "Solvolytic Displacement Reaction," McGraw-Hill Book Company, Inc., New York (1962).
21) *Cf.* A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); C. F. H. Tipper, *J. Chem. Soc.*, **1955**, 2045; P. von R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).
22) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corce, *ibid.*, **74**, 1113 (1952).
23) H. C. Brown, K. J. Morgan and F. J. Chloupek, *ibid.*, **87**, 2137 (1965).
24) H. C. Brown and S. Nishida, private communication.

the solvolysis rate by a factor of 2×10^4 as is shown in Table 2. Supposing that the unusual reactivity of the cyclopropylcarbinyl system is due to a resonance between the cyclopropane ring and an electron deficient center, such as a non-classical resonance or homoconjugation, the rearranged products should be formed, since the product distribution will be a qualitative reflection of the charge distribution in the intermediate.[25] In other words, if the charge localizes mostly on the tertiary reacting center, the rate-enhancement caused by the cyclopropyl function should be decreased markedly in the tertiary spiro cyclopropylcarbinyl system. The results obtained in the present study suggest that the positive charge in the intermediate is localized mostly at the reaction center and that, accordingly, the intermediate is essentially classical.

Therefore, it seems likely to be necessary to consider the contribution of another factor in order to establish the peculiarity of this system. Other spiro compounds are currently under investigation; the results will be reported in the near future.

Experimental[26]

Spiro[2, 4]heptan-4-one. A solution of 38.6 g of sodium dichromate dihydrate in 161 m*l* of water containing 52.5 g of concentrated sulfuric acid and 16.5 g of acetic acid was added to a solution of 36.0 g (0.321 mol) of spiro[2, 4]hept-4-ol in 200 m*l* of benzene. The temperature of the mixture was maintained below 5°C by an ice-salt bath. After the addition, the reaction mixture was stirred for additional two hours at room temperature. The aqueous layer was separated, diluted with 100 m*l* of water, and extracted with three 70 m*l* portions of benzene. These extracts were then combined with the original benzene layer, washed with a sodium carbonate solution, and dried over anhydrous magnesium sulfate. The solution was concentrated by distillation through a 15-cm Widmer column and distilled. Bp 87—89°C/63 mmHg (lit.[27] 54—55°C/14 mmHg), yield 25.0 g (71%), n_D^{25} 1.4688 (lit.[7] $n_D^{17.5}$ 1.4688). The NMR and IR spectra were in agreement with those previously reported. 2, 4-Dinitrophenylhydrazone, mp 155—156°C (lit.[42] 160—161°C).

Found: C, 53.75; H, 4.85; N, 19.25%. Calcd for $C_{13}H_{14}O_4N_4$: C, 53.79; H, 4.86; N, 19.30%.

4-Methyl Spiro[2, 4]heptan-4-ol. The ketone obtained above was reacted with 1.5 equi-molar methyl magnesium iodide and worked up in the usual manner. Bp 35—36°C/2.0 mmHg, yield 19.2 g (76%), n_D^{25} 1.4753. The IR spectrum showed the following bands (cm^{-1}); 3380(s), 3070(m, cyclopropane C–H stretch), 2945(s), 2870(s), 1450(s), 1378(s), 1186(s), 1098(s), 1014(s), skeletal vibration of the cyclopropane ring), and 902(s). The NMR spectrum contained the peaks expected for a methyl group (singlet, 9.05 τ) and a cyclopropyl group (two multiplets at *ca.* 9.45 and 9.69 τ).

Spiro[2, 5]octan-4-one. Spiro[2, 5]octan-4-ol was oxidized to the ketone following the procedure by which spiro[2, 4]heptanol was oxidized. Bp 83—85°C/24 mmHg, yield 75% and n_D^{25} 1.4712. The NMR spectrum showed the following peaks (τ): 7.70 (multiplet, area 2), 7.90—8.35 (complex multiplet, area 6), *ca.* 8.90 and 9.50(A_2B_2 pattern, area 4). The IR spectrum contained the following bands (cm^{-1}): 3080(w, cyclopropane C–H stretch), 2920(s), 2860(s), 1692(s, C=O stretch), 1452(s), 1360(s), 1119(s), 1020(s, skeletal vibration of the cyclopropane ring), 980(s), and 924(s). 2, 4-dinitrophenylhydrazone, mp 154—155°C.

Found: C, 54.98; H, 5.30; N, 18.41%. Calcd for $C_{14}H_{16}O_4N_4$: C, 55.25; H, 5.30; N, 18.41%.

4-Methyl Spiro[2, 5]octan-4-ol. 4-Methyl spiro-[2, 5]octan-4-ol was prepared by reacting the ketone obtained above with 1.5 equi-molar methyl magnesium iodide. Bp 48—49°C/3.0 mmHg, yield 87%, n_D^{25} 1.4810. The IR spectrum showed the following bands (cm^{-1}): 3400(s, O–H stretch), 3075(w, cyclopropane C–H stretch), 1447(s), 1373(s), 1120(s), and 1013(s, skeletal vibration of the cyclopropane ring). The NMR spectrum contained the peaks expected for a methyl group (singlet, 8.94 τ) and a cyclopropyl group (complex multiplets, 9.25 and 9.70 τ).

1, 2, 2-Trimethylcyclopentanol and 1, 2, 2-Trimethylcyclohexanol. 1, 2, 2-Trimethylcyclopentanol and 1, 2, 2-trimethylcyclohexanol were prepared by reacting the corresponding ketones obtained by the method reported in the previous paper[14] with excess methyl magnesium iodide in the usual manner. The physical properties were in agreement with those previously reported, and the spectra were fully consistent with the structure.

Preparation of *p*-Chlorobenzoates. The four tertiary *p*-chlorobenzoates, Ib, IIb, IIIb, and IVb, were prepared according to the procedure of Hart and Law,[4] and were purified by recrystallization from petroleum ether. The secondary *p*-chlorobenzoates, Vb and VIb, were obtained following the procedure of Sneen and Baron,[5] and were purified by repeating the distillation under reduced pressure. The NMR and IR spectra of esters were fully consistent with the structures. The physical properties and analytical data are given in Table 5.

Kinetic Measurements. *(a) Solvent.* Dioxane was purified following the procedure reported in the previous paper.[14]

(b) Procedure. Approximately 0.02 N solutions of ester were employed, and the reactions were followed by titrating the liberated *p*-chlorobenzoic acid potentiometrically to the pH 10 end point with a standard potassium hydroxide solution. The kinetic runs for the esters, Ib and IIb, were carried out following the procedure (c-1) described in the previous paper, while those for the esters, IIIb, IVb, Vb, and VIb, were accomplished by the (c-2) procedure. The data for a typical kinetic run are listed in Table 6.

Product Analysis. *(a) 4-Methyl Spiro[2, 4]hept-4-yl p-Chlorobenzoate.* A solution of 4-methyl spiro-[2, 4]-hept-4-yl *p*-chlorobenzoate (7.70 g, 0.0291 mol) in 290

25) *Cf.* G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

26) Melting points were uncorrected. NMR spectra were obtained with a JNM-4H-100. IR spectra were obtained with a Hitachi ESI-S2 infrared spectrophotometer. Hitachi-Horiba pH meter type M-4 was used to measure the solvolysis rate. Vpc analyses were performed on the Yanagimoto Gas Chromatograph model GCG-3.

27) M. Mayer and H. J. Schubert, *Chem. Ber.*, **91**, 768 (1958).

TABLE 5. PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR THE *p*-CHLOROBENZOATES

p-Chloro-benzoate	Mp or bp	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
Ib	26.5—27.5°C	68.05	68.24	6.47	6.51
IIb	49—50°C	68.93	69.00	6.87	6.85
IIIb	24—25°C	67.54	67.42	7.13	6.99
IVb	67—69°C	68.45	68.23	7.51	7.62
Vb	100—101°C/1×10^{-2} mmHg	67.22	67.03	6.05	6.17
VIb	113—114°C/7×10^{-3} mmHg	68.05	67.81	6.47	6.32

TABLE 6. SOLVOLYSIS OF 0.0193 M 4-METHYL SPIRO[2, 4]HEPT-4-YL *p*-CHLOROBENZOATE IN 85 WT% AQUEOUS DIOXANE AT 55.32±0.01°C

Time, sec	Base, m*l*[a)]	$k_1\times10^4$, sec^{-1}
—	0.280	—
492	1.113	4.34
725	1.470	4.43
994	1.792	4.32
1215	2.061	4.36
1442	2.282	4.30
1636	2.477	4.33
1933	2.735	4.33
2250	2.970	4.32
2612	3.188	4.27
3000	3.370	(4.17)
3423	3.585	(4.21)
∞	4.609[b)]	—
	Mean 4.33±0.03	

a) Volume of 0.0204 N potassium hydroxide solution per 4.840 m*l* aliquot.
b) 100.9% of theoretical.

m*l* of 85 wt% aqueous dioxane was maintained at 80—90°C for five hours; then it was cooled, and 250 m*l* of water was added. The reaction mixture was extracted with six 75-m*l* portions of *n*-hexane, and the combined extracts were washed with several portions of water in order to remove the dioxane. After the solution has been dried over anhydrous magnesium sulfate, the solvent was removed through a 15-cm Widmer column and concentrated to a volume of 30 m*l*. Vpc analysis (Apiezone Grease L on celite 30%, 2 m, 70°C) of the residual oil indicated that the solvolysis product consisted of three components (area ratio 12 : 25 : 63)[28)] with the retention times of 20.7, 27.7, and 64 min respectively. The retention time of the latest component was in agreement with that of the original alcohol, Ia. The distillation of the concentrated extracts gave two fractions: bp 70—90°C/130 mmHg, 1.2 g and bp 70—75°C/13 mmHg, 2.0 g. The NMR and IR spectra of the latter fraction were identical with those of 4-methyl spiro[2, 4]heptan-4-ol. The two components with the retention times of 20.7 and 27.7 min were isolated by preparative gas chromatography from the former fraction. The first component was identified as 4-methylene spiro[2, 4]heptane from the results of elemental analysis and from its spectral data (described under Results). Spectral data: NMR (CCl_4); 5.51 τ (triplet, J=2 cps, area 1), 5.83 τ (triplet, J=2 cps, area 1), 7.4—7.7 τ (complex multiplet, area 2), 8.15—8.40 τ (multiplet, area 4), and *ca.* 9.30 τ (multiplet, area 4): IR (neat, cm^{-1}); 3060(s), 2945(s), 2860(s), 1650(s), 1447(m), 1432(s), 1423(s), 1346(s), 1011(s), 948(s), 860(s), and several weak bands.

Found: C, 88.59; H, 11.32%. Calcd for C_8H_{12}: C, 88.82; H, 11.18%.

The second component was similarly identified as 4-methyl spiro[2, 4]hept-4-ene. Spectral data: NMR (CCl_4); 4.73 τ (multiplet, area 1), 7.5—7.8 τ (complex multiplet, area 2), 8.0—8.2 τ (partially-resolved multiplet at 8.04, 8.11, and 8.17 τ, total area 2), 8.65 τ (doublet, J=2 cps, area 3), *ca.* 9.35 τ multiplet, area 2), and *ca.* 9.55 τ (multiplet, area 2): IR (neat, cm^{-1}); 3055(m), 2925(s), 2860(s), 1646(w), 1444(s), 1380(s), 1304(w), 1111(m), 1044(m), 1017(m), 986(m), 949(s), 911(m), 864(m), and 809(s).

Found: C, 88.68; H, 11.38%; Calcd for C_8H_{12}: C, 88.82; H, 11.18%.

(b) 4-Methyl Spiro[2, 5]oct-4-yl p-Chlorobenzoate. A solution of 4-methyl spiro[2, 5]oct-4-yl *p*-chlorobenzoate (5.65 g, 0.0203 mol) in 200 m*l* of 85 wt% aqueous dioxane was refluxed for three hours and then worked up as has been described above. Vpc analysis (Apiezone Grease L on celite 30%, 2 m, 102°C) indicated that the solvolysis product was composed of three components (area ratio 4 : 34 : 62).[28)] These components were isolated by preparative gas chromatography. The latest component was identified as 4-methyl spiro[2, 5]-octan-4-ol through a comparison of its spectra and retention time with those of an authentic sample. The structure of the second component was identified as 4-methyl spiro[2, 5]octan-4-ene on the basis of the elemental analysis and the spectral data (described under Results). Spectral data: NMR (CCl_4); 4.65 τ (multiplet, area 1), *ca.* 7.98 τ(complex multiplet, area 2), 8.2—8.8 τ(complex multiplet together with a sharp doublet, J=2 cps, total area 7), *ca.* 9.28 τ(multiplet, area 2), and *ca.* 9.71 τ (multiplet, area 2): IR (neat, cm^{-1}); 3065(m), 2910(s), 2850(s), 1655(m), 1445(s), 1380(m), 1136(m), 1086(m), 1012(s), 919(s), 895(s), 793(s), and several weak bands.

Found: C, 88.36; H, 11.65%. Calcd for C_9H_{14}: C, 88.45; H, 11.55%.

Not enough of the first component could be collected for us to obtain the spectral data.

28) It was assumed that the molar response factor of olefin is 0.85 times that of alcohol in cyclopentyl derivative and 0.87 times in cyclohexyl derivative.