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SMALL RING COMPOUNDS—XVI

SOLVOLYSIS OF α-(*p*-SUBSTITUTEDPHENYL)CYCLOPROPYLCARBINYL *p*-NITROBENZOATE

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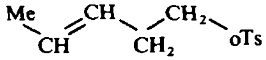
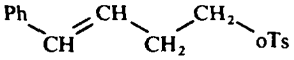
Abstract—α-(*p*-substitutedphenyl)cyclopropylcarbinyl *p*-nitrobenzoate (IV), α-(*p*-substitutedphenyl)isobutyl *p*-nitrobenzoate (VI) and α-methylcyclopropylcarbinyl *p*-nitrobenzoate (V) were synthesized and solvolyzed in 65% aqueous dioxan. The substituents studied were Me, Cl and OMe. A plot of the kinetic data obtained in the solvolysis of IV vs. σ^+ was linear with slope —3·61 at 30°. The structure of the transition state in the solvolysis has been discussed.

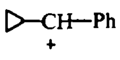
It is considered that the cyclopropylcarbinyl cation is stabilized by the delocalization of the positive charge.[1] Roberts[2] has suggested an unsymmetrical bicyclobutonium ion for the structure of the cation, while Schleyer[1] and others[3,4] have proposed a symmetrical bi-sected type ion. As the rate of solvolysis of I is twice as fast as that of II, Roberts has pointed out that in the bicyclobutonium-type ion formed from II, the stabilization of the cation by the Ph group through π-interaction is cancelled by the destabilization of the cation through the inductive electron withdrawing effect of the Ph group.[5] Thus the cation would not be a true benzylic-type cation. Consequently, in the bicyclobutonium ion if a Ph group is substituted on the α-position, the overlap between the π-orbital of the Ph group and that involved in the bicyclobutonium ion would not be enough to accomplish complete conjugative interaction.



I

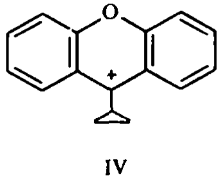


II



III

On the other hand, although a cyclopropyl group stabilizes a carbonium ion more than a Ph group as was observed in the solvolysis of II, the cyclopropyl group in the 9-cyclopropyl-9-xanthyl cation (IV) makes a smaller contribution to the stability of the cation.[6] These facts suggest that the character of the cyclopropylcarbinyl cation



IV

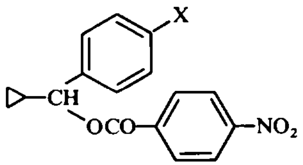
depends on the structure of the α-substituent. Thus three types are possible for the cation III:

(1) The overlap between the π-orbital of the Ph group and that involved in the cyclopropylcarbinyl group is enough to accomplish sufficient conjugative interaction. (For example: bi-sected ion).

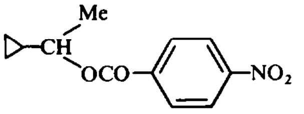
(2) The cation possesses a character similar to a benzylic cation and the cyclopropyl group may contribute only inductively. (For example: classical ion.)

(3) The positive charge is delocalized within the cyclopropylcarbinyl group and the resonance effect and the inductive effect of the Ph group may nearly counteract each other. (For example: bicyclobutonium ion.)

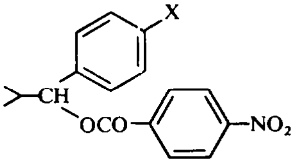
A series of α-(*p*-substituted phenyl) cyclopropylcarbinyl *p*-nitrobenzoates (IVa–d) were synthesized and the substituent effect on the solvolysis of IVa–d in 65% aqueous dioxan was studied for the purpose of determining the character of the α-phenylcyclopropylcarbinyl cation. If the cation is of type (3), some abnormality in the substituent effect* should be observed. Furthermore, α-methylcyclopropylcarbinyl *p*-nitrobenzoate (V) and α-(*p*-substituted phenyl) isobutyl *p*-nitrobenzoate (VIa–d) were synthesized and used to determine the difference in effect between Me and Ph groups or between cyclopropyl and isopropyl groups on solvolysis. The products of the solvolysis of IV were *p*-nitrobenzoic acid and the corresponding α-(*p*-substituted phenyl) cyclopropylcarbinol (VII), and no rearranged product was obtained. The kinetics of the solvolyses of IV, V and VI were of the first order. The results are shown in Tables 1 and 2. A plot of the kinetic data shown in Table 1 vs. σ^+ was linear with slope −3·61 at 30° (Fig. 1).



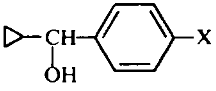
IVa: X = H
IVb: X = Me
IVc: X = Cl
IVd: X = OMe



V



VIa: X = H
VIb: X = Me
VIc: X = Cl
VId: X = OMe



VII

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* The substituent effect might be very small or a Hammett-type plot of the effect might not be linear.

TABLE 1. RATES CONSTANTS AND DERIVED DATA FOR THE SOLVOLYSIS OF IVa–d IN 65% AQUEOUS DIOXAN

Compound	Substituent	$k_1 \times 10^4$ sec^{-1}			Relative rate (30°)	ΔE kcal/mol	ΔS e.u.
		79·9°	30°	0°			
IVa	H	3·68	0·0189	—	1	22·4	−12·7
IVb	Me	22·5	0·206	0·0048	10·9	20·0	−16·0
IVc	Cl	1·52	0·00564	—	0·3	23·8	−10·4
IVd	OMe		14·8	0·358	780	20·4	−6·1

TABLE 2. RATES CONSTANTS FOR THE SOLVOLYSES OF V AND VIa–d IN 65% AQUEOUS DIOXAN

Compound	Substituent	$k_1 \times 10^8$ (79·9°) sec^{-1}
V	—	$3{\cdot}43 \times 10^2$
VIa	H	3·57
VIb	Me	8·88
VIc	Cl	2·85
VId	OMe	2870

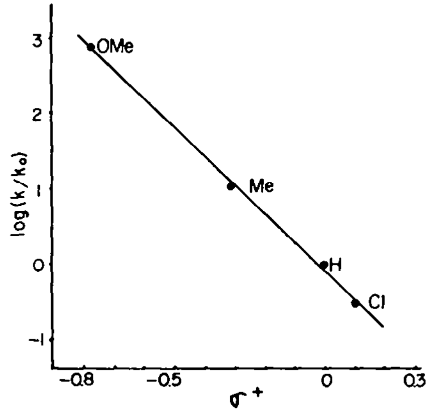

FIG. 1 Hammett-type plot for solvolysis of IVa–d in 65% aqueous dioxan at 30°.

As already mentioned, the rate of solvolysis of I being twice as fast as that of II, suggests that the transition state in the solvolysis of II is the bicyclobutonium ion. The results shown in Table 1 and 2, however, clearly indicate that a Ph substituent instead of a Me in the α-position of the cyclopropylcarbinyl cation produces a 100-fold rate increase. It thus appears that the transition state in the solvolysis of IV is not the same as that in the solvolysis of II, and that in the former transition state, the resonance and the inductive effects of the Ph group are not cancelled. Furthermore, the linear relationship between log k/k_0 and σ^+ (Fig. 1) would indicate no abnormality in the substituent effect and the ρ-value of −3·61 would be reasonable for the solvolysis of a benzylic type compound.[8]

The rate of solvolysis of IV is 10^4 times faster than that of VI which implies that the structure of the transition state in the solvolysis of IV is not the localized classical benzylic cation. These facts suggest that the α-phenylcyclopropylcarbinyl cation is of type (1) and the structure of the transition state in the solvolysis of II is of type (3). Consequently, it may be concluded that the structure of the cyclopropylcarbinyl cation is not the same as a non-classical cation formed from a carbonium ion and a double bond not conjugated with the carbonium ion.

EXPERIMENTAL

α-(p-*Substituted phenyl) cyclopropylcarbinol* (VII). *p*-Substituted phenyl cyclopropyl ketones, prepared from *p*-substituted phenyl γ-chloropropyl ketones, were reduced with LAH in anhyd ether to give VII. VIIa, b.p. 75–78°/4 mm, yield 80%; VIIb, b.p. 104–106°/3 mm, yield 75%; VIIc, b.p. 110°/3 mm, yield 77%; VIId, b.p. 121–123°/3 mm, yield 80%.

α-(p-*Substituted phenyl)isobutyl alcohols* (VIII). The title compounds were synthesized by a method similar to that used for VII. VIIIa, b.p. 63–68°/4 mm, yield 75%; VIIIb, b.p. 85–95°/3 mm, yield 71%; VIIIc, b.p. 93–100°/3 mm, yield 74%; VIIId, b.p. 111–112°/3 mm, yield 68%.

α-(p-*Substituted phenyl)cyclopropylcarbinyl* p-*nitrobenzoate* (IV) *and* α-(p-*substituted phenyl)isobutyl* p-*nitrobenzoate* (VI). The title compounds were synthesized from the corresponding alcohols and *p*-nitrobenzoyl chloride by the usual method[7] preparing the *p*-nitrobenzoate of alcohol. IVa, m.p. 84–85°, yield 61%, (Found: C, 68·54; H, 5·31; N, 4·99. $C_{17}H_{15}O_4N$ requires: C, 68·67; H, 5·08; N, 4·71%); IVb, m.p. 86–87°, yield 65%, (Found: C, 69·24; H, 5·57; N. 4·38. $C_{18}H_{17}O_4N$ requires: C, 69·44; H, 5·50; N, 4·50%); IVc, m.p. 90–92°, yield 68%, (Found: C, 61·89; H, 4·56; N, 4·47. $C_{17}H_{14}O_4NCl$ requires: C, 61·55; H, 4·25; N, 4·22%); IVd, m.p. 77–78°, yield 68%, (Found: C, 66·11; H, 5·24; N, 4·49. $C_{18}H_{17}O_5N$ requires: C, 66·05; H, 5·24; N, 4·28%); VIa, b.p. 166–170°/0·2 mm, yield 70%, (Found: C, 68·48; H, 6·01; N, 4·73. $C_{17}H_{17}O_4N$ requires: C, 68·21; H, 5·73; N, 4·68%); VIb, m.p. 62–63·5°, yield 65%, (Found: C, 69·29; H, 6·35; N, 4·48. $C_{18}H_{19}O_4N$ requires: C, 68·99; H, 6·11; N, 4·47%); VIc, m.p. 74–76°, yield 69%, (Found: C, 61·38; H, 4·87; N, 3·90. $C_{17}H_{16}O_4NCl$ requires: C, 61·16; H, 4·83; N, 4·19%); VId, m.p. 54–55°, yield 67%, (Found: C, 65·85; H, 5·91; N, 4·05. $C_{18}H_{19}O_5N$ requires: C, 65·64; H. 5·82; N, 4·25%).

α-*Methylcyclopropylcarbinyl* p-*nitrobenzoate* (V) was prepared from α-methylcyclopropylcarbinol and *p*-nitrobenzoyl chloride by the usual way,[7] b.p. 141–143°/3 mm, m.p. 55–56°, yield 77%. (Found: C, 60·64; H, 6·46; N, 6·08. Calcd. for $C_{12}H_{15}O_4N$: C, 60·75; H, 6·37; N, 5·90%.)

Kinetic experiments

The rates of the solvolysis of the *p*-nitrobenzoate esters in 65% aqueous dioxan were determined using solns about 0·015M in *p*-nitrobenzoate ester and titrating the liberated *p*-nitrobenzoic acid with 0·015N NaOH in 65% dioxan to a phenolphthalein end point. The solvolysis of VIa–d was carried out by means of the ampule technique. The base was frequently restandardized against benzoic acid during the course of the work.

REFERENCES

[1] For a summary of leading references see P. R. Schleyer and G. W. VanDine, *J. Am. Chem. Soc.* **88**, 2321 (1966).

[2] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *J. Am. Chem. Soc.* **81**, 4390 (1959).

[3] N. Deno, *Progr. Phys. Org. Chem.* **2**, 129 (1964).

[4] H. G. Richey, Jr., and J. M. Richey, *J. Am. Chem. Soc.* **88**, 4971 (1966).

[5] K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.* **87**, 1331 (1965).

[6] N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln and J. O. Turner, *J. Am. Chem. Soc.* **87**, 4533 (1965).

[7] R. A. Sneen and A. L. Baron, *J. Am. Chem. Soc.* **83**, 614 (1961). Sneen and Baron[7] also discussed on a difference of the character between a cyclopropylcarbinyl and a cholesteryl cations.

[8] N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.* **79**, 5804 (1957).