4. D. Bratko, L. B. Bhuiyan, and C. W. Outhwaite, *J. Phys. Chem.*, **90**, 6248 (1986); C. W. Outhwaite, and L. B. Bhuiyan, *J. Chem. Phys.*, **84**(6), 3461 (1986); Christopher, W. Outhwaite, *J. Chem. Soc., Faraday Trans.*, 2, **82**, 789 (1986); C. Caccamo, G. Pizzimenti, and L. Blum, *Phys. Chem. Liq.*, **14**, 311 (1985); *J. Chem. Phys.*, 84(6), 3327 (1986).
5. O. Rice, *Phys. Rev.*, **31**, 1051 (1928); R. Kofman, R. Garrigos, and P. Cheyssac, *Thin Solid Films* **82**, 73 (1981).
6. Wolfgang Schmickler and Douglas Henderson, *J. Chem. Phys.*, **85**(3), 1650 (1986); G. A. Martynov and R. R. Salem, *Lecture Notes in Chemistry*, Vol. 33; "Electrical Double Layer at a Metal-dilute Electrolyte Solution Interface", Springer-Verlag, New York (1983); Ezequiel Leiva and Wolfgang Schmickler, *J. Electroanal. Chem.*, **229**, 39 (1987); A. Hamelin, L. Stoicoviciu, and F. Silva, *J. Electroanal. Chem.*, **229**, 107 (1987).
7. F. Chao, M. Costa, R. Cherrak, J. Lecouer, and J. P. Bellier, *J. Electroanal. Chem.*, **229**, 19 (1987).
8. J.O'M. Bockris, B. E. Conway, and E. Yeager, *Comprehensive Treatise of Electrochemistry*, Vol. 1: "Double Layer", Chap. 3, Plenum Press, New York and London (1980); A. W. Adamson, *Physical Chemistry of Surfaces*, 4th ed., Chap. 5, John Wiley & Sons. Inc., New York (1982).
9. D. M. Mohilner, *Electroanalytical Chemistry*, Vol.1, "The Electrical Double Layer, Part I." ed. A. J. Bard, Chap. 3, Marcel Dekker, Inc., New York (1966).
10. S. Y. Kim (Ph.D. Thesis, Pennsylvania State University).
11. C. Kittel, *Introduction to Solid State Physics*, 5th ed., John Wiley & Sons, Inc., New York (1976).
12. D. M. Kolb, *J. Vac. Sci. Technol.*, **A4**(3), 1294 (1986); D. M. Kolb, and J. Schneider, *Surf. Sci.*, **162**, 764 (1986).

^{13}C NMR Study of the Application of the "Tool of Increasing Electron Demand" to the 9-Aryl-tricyclo[3.3.1.$0^{2,8}$]non-9-yl, and 8-Aryl-Tetracyclo[3.2.1.$0^{2,7}$.$0^{4,6}$]oct-8-yl cations

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The ^{13}C NMR shifts of a series of para-substituted 9-aryl-tricyclo[3.3.1.$0^{2,8}$]non-9-yl and 8-aryl-tetracyclo[3.2.1.$0^{2,7}$.$0^{4,6}$]-oct-8-yl cations were measured in FSO_3H/SO_2ClF at -90 °C or -70 °C in order to examine whether the ρ^{c+} values can be use to explain the mechanism for the stabilization of the geometrically rigid cyclopropylcarbinyl cations. Plots of the $\Delta\delta^{c+}$ shifts against σ^{c+} reveal excellent linear correlation. The tricyclononyl systems yield a ρ^{c+} value of -4.95 with a correlation coefficient $r = 0.9948$. The tetracyclo-octanyl systems give a ρ^{c+} value of -6.39 with $r = 0.9943$. A fair parallelism exists between the results of ^{19}F nmr studies and the change of ρ^{c+} values in these cations. Accordingly, the present study established that the ρ^{c+} value can be used as a mearsure of the geometric influence for the charge delocalization in cyclopropylcarbinyl cations.

Introduction

The use of the Hammett σ and Brown σ^+ substituent constants in the investigation of structure-reactivity relationships is well established[1]. These substituent constants provide a measure of the stabilizing effect of the substituent on the reaction center of the transition state in the solvolytic and related reaction. On the basis of the usual assumption of a late transition state[2] in such solvolytic reactions, it was reasonable to anticipate that these constants could also be used to correlate that stabilities of the carbocationic intermediates produced in such solvolyses.

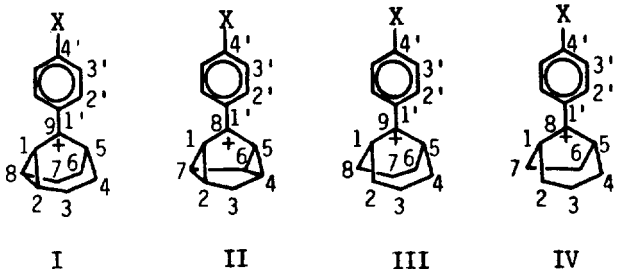
In recent years it has become possible to prepare and observe such carbocations in superacid media[3]. The ^{13}C NMR chemical shifts in such carbocations have been taken to measure the electron delocalization of the carbocation. Accordingly, numerous attempts seeking to correlate the ^{13}C NMR shifts with σ^+, electrophilic substituent constant, have been reported[4].

On the assumption of (*i*) a late transition state for the solvolysis of cumyl chlorides in acetone and (*ii*) that the ^{13}C chemical shifts were linearly proportional to charge density, it was not unreasonable to expect the σ^+ constants to correlate ^{13}C shifts of the fully formed carbocations in superacid. Thus Olah and coworkers plotted the ^{13}C cationic carbon chemical shifts δC^+ of cumyl cations against the electrophilic substituent constant(σ^+ and noted an approximate linear correlation[5]. In a reinvestigation of the behavior of the substituted *tert*-cumyl cations, Kelly and Spear[6] observed a lower correlation coefficient, $r = 0.967$. Even more importantly, they pointed out that the least-square line for their data failed to pass through the point for the parent *tert*-cumyl cation. They suggested that the discrepancy might be due to an enhanced charge delocalization in ions containing electron donating substituents.

Therefore, Brown[7] and coworkers proposed the following modified Hammett-Brown equation of the form

$$\Delta\delta^{c+} = \rho^{c+}\sigma^{c+}$$

where $\Delta\delta^{c+}$ is the difference between the cationic carbon



I II III IV

Figure 1.

chemical shift for the unsubstituted cation and that for the substituted cation species, *e.g.*, $\Delta\delta^{c+} = [\delta C^+(X=H) - \delta C^+(X=Z)$, and σ^{c+} is the enhanced new substituent constant. A plot of these σ^{c+} value against $\Delta\delta^{c+}$ values of the 1-aryl-1-cyclopentyl cation revealed an excellent correlation with $r = 0.9999$ and $\rho^{c+} = -16.84$. When applied to a range of acyclic, cyclic, and polycyclic dialkylaryl systems, these new σ^{c+} constants give also excellent linear correlation for the cationic carbon substituent chemical shifts ($\Delta\delta^{c+}$). Consequently, it may be possible to use the ρ^{c+} values as a measure of electronic interaction or geometric influence for charge delocalization in carbocations.

It is of interest to examine the structural effect on relative stability of rigid cyclopropylcarbinyl cations using ρ^{c+} values. Moreover, it is of major interest to test whether the ρ^{c+} values can be used to explain the mechanism for stabilization of geometrically rigid cyclopropylcarbinyl cations. Accordingly, we selected the 9-aryl-tricyclo[3.3.1.$0^{2,8}$]non-9-yl (I) and 8-aryl-tetra-cyclo[3.2.1.$0^{2,7}$.$0^{4,6}$] oct-8-yl cation (II), shown in Figure 1. The substituents X in benzene ring were varied over the usual range (X = *p*-CH_3O, *p*-CH_3, *p*-F, *p*-Cl, *p*-H) to provide a wide variation in electron demand in terms of ρ^{c+}.

The cyclopropane ring in the geometrically rigid cation such as ion 1 is situated in a favored bisected conformation toward the vacant *p*-orbital at the cationic carbon for the maximum charge delocalization. In contrast, the cyclopropane ring in ion 2 does not maintain the favored bisected orientation.

Results and Discussion

The precursor alcohols, 9-aryl-tricyclo[3.3.1.$0^{2,8}$]nonan-9-ol, 8-aryl-tetracyclo[3.2.1.$0^{2,7}$.$0^{4,6}$]octan-8-ol, were prepared by the addition of the corresponding ketone to the Grignard reagents prepared from the corresponding bromobenzenes. The cations were prepared by adding a measured quantity of the alcohol to the FSO_3H/SO_2ClF solution at −100 °C. The ^{13}C chemical shifts were then measured at −90 °C. The ^{13}C chemical shifts of the these cations are summarized in Table 1 with the corresponding alcohols.

A plot of the new substituent constants, σ^{c+}, against $\Delta\delta^{c+}$ value for ion 1 revealed an excellent correlation with $r = 0.9948$ and $\rho^{c+} = -4.95$ (Figure 2), and it gives also an excellent correlation for ion 2 with $r = 0.9943$ and $\rho^{c+} = -6.39$ (Figure 3).

When the ρ^{c+} value of ion 1 is compared to that of ion 2, the ion 1 shows the low ρ^{c+} value (−4.95). The less negative slope ρ^{c+} might indicate a lower electron demand in the fully developed cations. This can be accounted for on the basis of

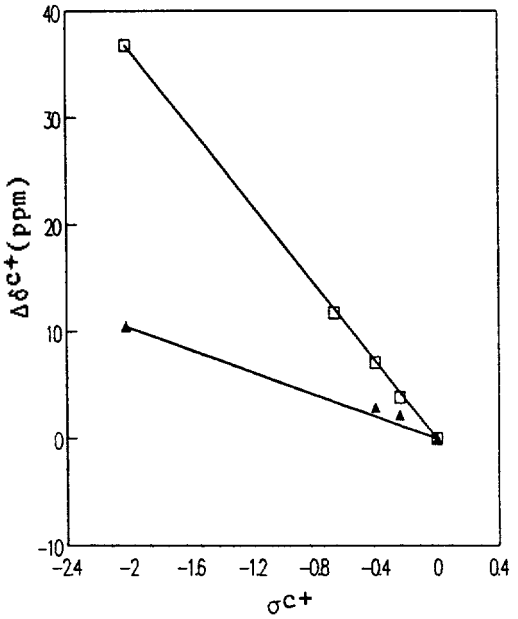


Figure 2. A plot of σ^{c+} values against $\Delta\delta^{c+}$ for ion 1 (△) (slope $\rho^{c+} = -4.95$, correlation coefficient = 0.9948) and for ion 3 (□) (slope $\rho^{c+} = -18.31$, correlation coefficient = 0.9998).

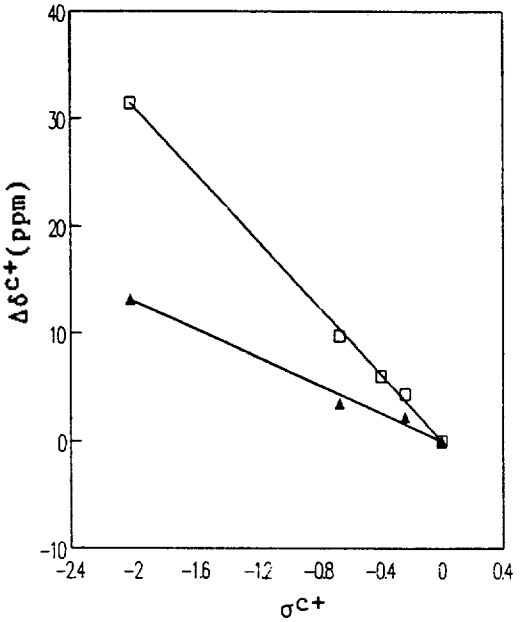


Figure 3. A plot of σ^{c+} values against $\Delta\delta^{c+}$ for ion 2 (△) (slope $\rho^{c+} = -6.39$, correlation coefficient = 0.9943) and for ion 4 (□) (slope $\rho^{c+} = -15.48$, correlation coefficient = 0.9993).

lesser electron demand to the substituted phenyl ring because of greater electron supply by the cyclopropyl group in ion 1. From this result, it suggested that cyclopropyl group in ion 1 supply electrons to the electron-deficient center more effectively than that of ion 2. In the case of ion 2, however, we would expect that the ρ^{c+} value for ion 2 reveals less negative value since the skeleton of this cation consists of two cyclopropyl groups. Indeed, an examination of molecular model shows that the cyclopropane ring in ion 1 is situated in a favored bisected conformation toward the vacant *p* orbital at the cationic center for the maximum charge delocalization while

Table 1. ^{13}C NMR Shifts of Ion 1, 2, 3, and 4 in FSO_3H/SO_2ClF at -90 °C or -70 °C

Ion	Substituent	chemical shift												
		C_9	C_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_1	C_2	C_3	C_4
I	*p*-OCH_3	238.6	70.7	57.6	70.7	42.8	18.6	41.8	18.6	42.8	132.0	138.6	129.3	173.8
		(72.5)	(14.1)	(16.0)	(14.1)	(22.8)	(25.6)	(40.6)	(25.5)	(22.8)	(140.7)	(127.7)	(113.3)	(158.6)
	p-F	242.2	84.4	58.2	84.4	41.9	19.7	43.7	19.7	41.9	136.0	133.2	118.9	172.6
		(72.3)	(13.9)	(16.6)	(13.9)	(22.4)	(25.0)	(40.4)	(25.0)	(22.4)	(143.8)	(127.5)	(114.3)	(161.6)
	p-Cl	242.9	87.1	60.4	87.1	43.8	19.9	42.3	19.9	43.8	133.2	134.8	131.4	150.2
		(72.8)	(14.2)	(17.2)	(14.2)	(22.8)	(25.4)	(40.7)	(25.4)	(22.8)	(146.9)	(128.1)	(127.7)	(132.7)
	p-H	245.1	85.8	59.5	85.8	43.8	19.8	42.2	19.7	43.8	132.1	136.4	130.9	142.9
		(73.0)	(14.1)	(17.2)	(14.1)	(22.8)	(25.5)	(40.7)	(25.5)	(22.8)	(148.4)	(127.9)	(126.1)	(126.8)
II	*p*-OCH_3		224.1	41.5	46.7	29.5	46.7	41.5	55.2	55.2	129.8	140.6	117.3	174.8
			(82.5)	(35.5)	(26.7)	(26.3)	(26.7)	(35.5)	(24.9)	(24.9)	(140.8)	(125.9)	(113.5)	(158.4)
	p-CH_3		233.7	44.8	50.8	30.6	50.8	44.8	62.6	62.6	133.5	136.2	132.1	160.4
			(82.7)	(35.6)	(26.9)	(26.3)	(26.9)	(35.6)	(25.1)	(25.1)	(145.6)	(128.8)	(124.7)	(136.2)
	p-Cl		235.0	46.9	53.4	31.3	53.5	46.9	66.7	66.7	133.6	136.5	131.6	152.3
			(82.5)	(35.7)	(27.0)	(26.4)	(27.9)	(35.7)	(25.2)	(25.2)	(146.9)	(128.2)	(126.4)	(132.5)
	p-H		237.2	46.6	53.0	31.2	53.0	46.6	66.2	66.2	135.2	135.5	131.1	144.6
			(82.8)	(35.6)	(27.0)	(26.4)	(27.0)	(35.6)	(25.2)	(25.2)	(148.5)	(128.1)	(124.3)	(126.7)
III	*p*-OCH_3	241.7	40.5	44.9	40.5	21.9	40.5	44.8	40.5	21.9	119.6	142.2	129.8	162.8
		(73.9)	(30.7)	(38.5)	(33.0)	(24.8)	(33.0)	(38.5)	(30.7)	(24.5)	(133.2)	(123.2)	(111.3)	(152.6)
	p-CH_3	266.7	43.8	49.8	43.8	22.3	43.8	49.8	43.8	22.3	124.9	138.2	134.9	173.4
		(73.8)	(27.2)	(35.4)	(28.5)	(20.9)	(28.5)	(35.4)	(27.2)	(20.7)	(142.2)	(129.1)	(124.2)	(136.5)
	p-Cl	274.6	45.5	52.2	45.5	22.4	45.5	52.2	45.5	22.4	135.2	138.4	133.7	164.6
		(73.8)	(27.1)	(35.5)	(29.5)	(20.8)	(29.5)	(35.5)	(27.1)	(20.4)	(143.7)	(128.6)	(127.1)	(132.6)
	p-H	278.5	45.7	52.5	45.7	22.5	45.7	52.6	45.7	22.5	137.2	137.8	133.1	154.7
		(74.2)	(27.3)	(35.5)	(29.7)	(20.9)	(29.7)	(35.5)	(27.3)	(20.6)	(145.1)	(128.6)	(125.4)	(127.2)
IV	*p*-OCH_3		239.4	48.6	25.9	18.3	25.9	48.6	47.9	47.9	119.3	145.3	126.3	161.9
			(79.9)	(48.6)	(25.9)	(18.3)	(25.9)	(48.6)	(47.9)	(47.9)	(138.5)	(126.5)	(113.7)	(158.7)
	p-CH_3		261.2	53.8	25.9	18.7	25.9	53.8	52.6	52.6	130.6	141.3	134.3	172.3
			(80.1)	(41.1)	(25.4)	(17.2)	(25.4)	(41.1)	(27.1)	(27.1)	(143.3)	(128.9)	(125.2)	(136.6)
	p-Cl		266.6	55.8	25.1	18.0	25.1	55.8	53.9	53.9	129.9	140.6	132.8	162.3
			(80.1)	(41.2)	(25.3)	(17.0)	(25.3)	(41.2)	(27.0)	(27.0)	(144.7)	(128.4)	(126.9)	(133.0)
	p-H		270.9	57.1	26.1	18.9	26.1	57.1	55.0	55.0	132.6	141.1	133.2	153.8
			(80.4)	(41.1)	(25.4)	(17.2)	(25.4)	(41.4)	(27.1)	(27.1)	(146.2)	(128.3)	(125.4)	(127.3)

[a] ^{13}C chemical shifts of corresponding alcohols are given in parentheses. [b]Chemical shifts are ± 0.1 ppm from external Me_4Si. [c]C_9 is cationic carbon for ion 1 and 3, C_8 is that for ion 2 and 4. [d]Assignment may be interchanged.

the cyclopropane ring in ion 2 does not maintain favored bisected orientation. However, the degree of charge delocalization by adjacent cyclopropane ring in ion 1 can not be directly compared with that of ion 2 using ρ^{c+} value because of the difference in the ring size of the two cations.

It was pointed out early that alicyclic compounds exhibit considerable changes in reactivity with changes in the number of carbon atoms in the ring[8]. This is true for both S_N2 and S_N1 reactions, as well as for the reaction of cyclic ketons. Indeed, Brown and coworkers[9] confirmed that a fair parallelism exists between a change of ρ^{c+} value for alicyclic cation systems and their ring size.

Therefore, we have prepared the model cations with the identical ring size but devoid of cyclopropane ring such as ion 3 and 4, shown in Figure 1. 9-Aryl-bicyclo[3.3.1.]non-9-yl (3) and 8-aryl-bicyclo[3.2.1.]oct-8-yl (4) cations were also generated from corresponding alcohols in FSO_3H/SO_2ClF solution at -100 °C, and the ^{13}C nmr spectra of these cations were recorded at -70 °C.

A plot of the $\Delta\delta^{c+}$ shifts against the σ^{c+} constants gave an excellent correlation for ion 3 ($\rho^{c+} = -18.31$, $r = 0.9998$) (Figure 2) and for ion 4 ($\rho^{c+} = -15.48$, $r = 0.9993$) (Figure 3). The ρ^{c+} values for ion 1, 2, 3, and 4 are summarized in Table 2.

There is 13.36 ($\Delta\rho^{c+}$) difference between the ρ^{c+} value for ion 1 and that of ion 3 in which the identical ring size but devoid of cyclopropyl group and the corresponding value between ion 2 and ion 4 is 9.09 ($\Delta\rho^{c+}$). Thus the result implys that the cation 1 is less sensitive to the variation of electron supply from the substituent of aromatic ring than ion 2. The Gassman-Fentiman[10] approach provides an alternative means of evaluating the electron deficiency of the developing cationic center in a system under-going ionization. The greater should be the demand on the aromatic ring for electronic stabilization. From the difference of $\Delta\rho^{c+}$ value these cations, it can be suggested that the charge delocalization into cyclopropane ring in ion 1 is greater than that of ion 2.

From previous ^{19}F nmr study[11], we confirmed that the orientation of the cyclopropane ring to the developing *p* orbital

Table 2. Comparison of ρ^{c+} Values and ^{19}F Chemical Shifts for Cation 1, 2, 3, and 4 in FSO_3H/SO_2ClF at −90 °C or −70 °C

Compound	$\delta^{19}F$	ρ^{c+}	Compound	$\delta^{19}F$	ρ^{c+}
 I	−86.2	−4.95 (0.9948)	 II	−81.5	−6.39 (0.9943)
 III	−64.8	−18.31 (0.9998)	 IV	−67.1	−15.48 (0.9993)
$\Delta\delta^{19}F = 21.4$		$\Delta\rho^{c+} = 13.36$	$\Delta\delta^{19}F = 14.4$		$\Delta\rho^{c+} = 9.09$

[a] ^{19}F chemical shifts are in ppm from external CCl_3F. [b]Correlation coefficient(r) in parenthese. [c]R denote para-substituted phenyl group.

at cationic carbon is a very important factor to stabilization of the geometrically rigid cyclopropylcarbinyl cations. In order to compare the ^{19}F chemical shift of ion 1 and 2, *p*-fluorophenyl substituted these cations were also prepared from the corresponding alcohols in FSO_3H/SO_2ClF at −100 °C and ^{19}F chemical shifts of the cations recorded at −70 °C. The chemical shift of the fluorine atom in ion 1 appears at −86.2 ppm and in ion 2 at −81.5 ppm. The signal of the fluorine atom in ion 1 was shifted considerably upfield (4.7 ppm) compared to that of ion 2. However, the degree of charge delocalization into cyclopropane ring in ion 1 can not be directly compared with that in ion 2 because the ring size of cyclic systems may influence the ^{19}F chemical shifts. Thus we have prepared the model cation 3 and 4 with essentially identical ring size, and their ^{19}F nmr data for these cations as well as $\Delta\delta$-value are summarized in Table 2.

The advantages of ^{19}F nmr spectroscopy are the great sensitivity to electron demand of the adjacent cationic center, and comparative insensibility to magnetic anisotropy of the solvent[12]. When a positive charge is dispersed into an adjacent *p*-fluorophenyl ring, the chemical shift of the fluorine atom on the phenyl ring moves downfield compared to that of uncharged species. Less efficient charge delocalization in *p*-fluorophenyl ring of carbocation should be the result in large charge dispersion into neighboring substituent. Thus, the ^{19}F nmr data can provide an important information on the degree of charge delocalization through neighboring group participation. The difference of ^{19}F chemical shift between ion 1 and 3 was 21.4 ppm, and the corresponding value between ions 2 and 4 was 14.4 ppm, respectively. This means that the signal of the fluorine atom in ion 1 was shifted considerably upfield ($\Delta\Delta\delta$, 7.0) compared to that of the ion 2. Consequently, the large $\Delta\delta^{19}F$ value (21.4 ppm) in case of the ion 1 compared to that of the ion 2 (14.4 ppm) is assumed to be due to the greater charge delocalization into adjacent cyclopropane ring. In our previous nmr studies on relative stability of carbocation species, the results of ^{19}F chemical shifts were in accord with the results of solvolytic studies.

In conclusion, both the application of the tool of increasing electron demand and the result of ^{19}F nmr study for ion 1 and 2 unambigously support the early conclusion that the conformation of cyclopropyl group is a very important factor for delocalization of the charge of the developing cationic center into adjacent cyclopropane ring. Moreover, the excellency of the correlation of ρ^{c+} value with the results of ^{19}F nmr data in the series of cations 1–4 confirmed that the ρ^{c+} value can be use to explain the mechanism for stabilization of geometrically rigid cyclopropyl-carbinyl cations.

Experimental Section

NMR Spectra. The ^{13}C nmr spectra were recorded at −90 °C or −70 °C on a Bruker AC-80 spectrometer operating at 20.1 MHz in the FT mode in 10-mm tube. Data were accumulated by using 32768 data points, spectral widths of 5000 or 6000 Hz, and pulse angles of 60°. Chemical shifts are reported ppm from external $(CH_3)_4Si$. Assignments were based on DEET-AU Program.

Carbocations. The cations were prepared by slow addition of a solution of the alcohols (*ca.* 150 mg) in dichloromethane-d_2 to a rapidly stirred solution of FSO_3H/SO_2ClF at −100 °C using a cation generation apparatus. The resulting concentration of the cationic solution were in the range 0.3–0.5 M and are shown generally yellow-brown.

Synthesis of Alcohols. A substituted 9-Aryl-tricyclo[3.3.1.$0^{2,8}$]nonan-9-ol, 8-aryl-tetracyclo[3.2.1.$0^{2,7}$.$0^{4,6}$]octan-8-ol, 9-aryl-bicyclo[3.3.1]nonan-9-ol, and 8-aryl-bicyclo[3.2.1]octan-8-ol were prepared by the addition of the corresponding ketone to *Grignard* reagent prepared from the corresponding substituted bromobenzene, and these carbinols were purified by column chromatography. All of these alcohols gave satisfactory ^1H and ^{13}C nmr spectra, and their ^{13}C chemical shifts are summarized in Table 1.

Synthesis of Ketones. Tricyclo[3.3.1.$0^{2,8}$]nona-9-one. 4-Cyclohepten-1-carboxylic acid is prepared from cyclopentanone by the four step devised by Stork *et al.*[13] The diazoketone, which is obtained from the corresponding acid chloride in the usual way, is converted to the tricyclic ketone by treatment with copper powder. ^1H nmr ($CDCl_3$) (ppm); 1.5–2.3 (m, 12H): IR (CCl_4) (cm^{-1}); 3050 (w), 2940 (s), 2865 (s), 1700 (s), 1450 (m), 1360 (m), 1240 (w), 910 (m), 450 (m).

Tetracyclo[3.2.1.$0^{2,7}0^{4,6}$]octa 8-one. The ketone was prepared by known procedures[14]. 3-Bromobicyclo[3.2.1]octa-2,6-diene is obtained from the reaction of norbornadiene and bromoform in the presence of TEBAC in 50% KOH solution, and was converted to the tribromobicyclo[3.2.1]octa-2-ene, and was hydrolyzed with mixture of ethanol-sulfuric acid, and was cyclized to ketone by heating with *tert.*-butoxide at 50 °C. ^1H NMR ($CDCl_3$) (ppm); 2.4 (m, 2H), 2.2 (t, 1H), 2.1 (s, 1H), 1.9 (m, 2H), 1.6 (m, 2H): IR (CCl_4) (cm^{-1}); 3050 (m), 2930 (m), 2860 (m), 1820 (s), 1350 (m), 1320 (w), 1200 (m), 1190 (m), 1170 (w), 1080 (w), 1050 (w), 970 (m), 880 (s).

Bicyclo[3.3.1]nona-9-one. The ketone was prepared according to publisched procedure[15]. Enamine, is prepared from cyclohexanone and morpholin in the usual way, reacted with acrolein to give amino ketone, and protected the keto group by ethylene glycol, and was converted to the N-oxide with hydrogenperoxide. By Hofmann rearrangement of N-oxide was obtained the bicyclo[3.3.1]nona-2-en-9-ethylene ketal, and hydrogenation of double bond under the catalyst of Pd/C. Ketal was hydrolyzed with aq. HCl to give the ketone ^1H NMR ($CDCl_3$) (ppm); 1.5 (m, 4H), 2.3 (m, 8H), 2.5 (m, 2H): IR (CCl_4) (cm^{-1}); 2980 (m), 2910 (s), 2860 (m), 1720 (s), 1450 (m), 1210 (m), 1080 (m), 950 (m), 820 (m).

Bicyclo[3.2.1]octa-8-one. The synthesis of this ketone follows that of the bicyclo[3.3.1]nona-9-one. The starting enamine was prepared from cyclopentanone and morpholine. ^{1}H NMR ($CDCl_3$) (ppm); 1.5 (m, 10H), 2.2 (m, 2H): IR (CCl_4) (cm^{-1}); 3000 (m), 2940 (s), 2860 (s), 1710 (s), 1630 (m), 1408 (m), 1353 (m), 1233 (m), 1195 (m), 1129 (s), 1105 (m), 960 (m), 800 (m).

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References

1. I. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1955).
2. G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
3. G. A. Olah, Angew. Chem., *Int. Ed. Engl.*, **12**, 173 (1973).
4. G. A. Olah, G. Liang and K. G. S. Prakash, *J. Am. Chem. Soc.*, **99**, 5683 (1977).
5. G.A. Olah, R. D. Porter, C. L. Jeuell and A. M. White, *J. Am. Chem. Soc.*, **94**, 2044 (1972).
6. D. P. Kelly and R. J. Spear, *Aust. J. Chem.*, **31**, 1209 (1978).
7. (a) H. C. Brown, D. P. Kelly and M. Perasamy, *Proc. Natl. Acad. Sci.*, **77**, 6956 (1980); (b) H. C. Brown, M. Perisamy, T. Perumal and D. P. Kelly, *J. Am. Chem. Soc.*, **106**, 2359 (1984).
8. H. C. Brown and K. Tidwell, *J. Am. Chem. Soc.*, **90**, 2691 (1968).
9. H. C. Brown and M. Perisamy, *J. Org. Chem.*, **46**, 3161 (1981).
10. P. G. Gassman and A. F. Fentiman, *J. Am. Chem. Soc.*, **92**, 2549 (1981).
11. (a) H. W. Shin and J. H. Shin, *Bull. Korean Chem. Soc.*, **8**, 144 (1987); (b) J. C. Shim, G. S. Nam and J. H. Shin, *Bull. Korean Chem. Soc.*, **10**, 132 (1989).
12. H. Guenther, NMR Spectroscopy, John Wiley & Sons, 1979.
13. G. Stork, A. Brizzolara and R. Rerrel, *J. Am. Chem. Soc.*, **85**, 207 (1963).
14. (a) W. R. Moore, W. R. Moser and J. E. Laprade, *J. Org. Chem.*, **28**, 2200 (1963); (b) N. A. LeBel and R. N. Liesemer, *J. Am. Chem. Soc.*, **87**, 4301 (1965).
15. G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5129 (1956).

Catalytic Properties of Phospholipase D using Phosphatidic Acid as an Activator

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The effects of phosphatidic acid(PA) on the activity of phospholipase D were examined in detail. The enzyme activity was examined in the liposome system containing phosphatidylcholine and PA, which was suspended in a desired buffer solution by ultrasonication. The substrate of large unilamella vesicle (LUV) state by ultrasonication was more effective on the enzyme activity than that of multilamella vesicle(MLV) by water-bath type sonication. The most effective molar ratio of PC-PA liposome for enzyme activity was found to be 1:0.7. The other optimum conditions were found 5 mM Ca^{2+} ion, pH 6.6, and incubation temperature of 27 °C. K_m and V_{max} values were estimated to be 1.43 mM and 0.8 nmole/min/μg protein respectively. These properties in a PC-PA liposome system were compared with those in a PC-SDS mixed micelle system. The effects of other phospholipids and organic phosphates on the enzyme activity were also examined.

Introduction

Phospholipase D (phosphatidylcholine phosphatido hydrolase, EC.3.1.4.4) catalyzes the hydrolytic cleavage of the terminal phosphate diester bond of glycerophosphatides containing choline, ethanolamine, serine or glycerol, resulting in the formation of phosphatidic acid. The enzyme also mediates transphosphatidylation by which the phosphatidyl group of phosphatidylcholine is transferred to alcohols. Phospholipase D occurs widely in the tissues of higher plants and especially in those of the genus Brassica.[1,2] In mammlian tissues, phospholipase D is enriched in the microsomal fraction of brain and lung tissues.[3,4] Taki *et al.* detected the enzyme activity in rat liver.[5] It appears to exist in plant cells in an insoluble form associated with plastids[6] but a soluble form can readily be demonstrated in cabbage[1], carrot[2], and cotton seed.[7] The enzyme in dry peanut shows the properties similar to those of the cabbage enzyme.[8]

The activities of the soluble enzyme of carrot and cabbage are stimulated by the addition of various organic solvents such as linear aliphatic ethers especially diethylether, ketones and esters,[2] except the phospholipase D of cotton seed which is not activated by diethylether.[6] Besides showing this solvent activation, the soluble enzyme from cabbage was stimulated by acidic phospholipid, phosphatidylinositol.[9] These observations on the stimulatory effects of solvents and surface active lipids suggest that the rates of enzyme hydrolysis are largely dependent on the physical states of the lipid