Solvolysis of 1-[*trans*-2-(*m*- or *p*-Substituted Phenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoates[1)]

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The solvolyses of 1-[*trans*-2-(*m*- or *p*-substituted phenyl)cyclopropyl]-1-methylethyl *p*-nitrobenzoates in 80% aqueous acetone have been studied with regard to both reactivity and product composition. For the less reactive substituents such as *m*-Br, *m*-Cl, and *m*-CF_3, the solvolysis products were the corresponding 2-(2-arylcyclopropyl)-2-propanol, indicating the cyclopropylmethyl cation intermediate. The ring-opened products increased as the electron-donating ability of the substituents increased. The application of the Yukawa–Tsuno equation to the reactivity afforded a ρ value of -1.43 and r value of 0.59 with a correlation coefficient of 0.997. A large value of r indicates the presence of the allylic cation intermediate where much more charge develops at the benzylic carbon for the derivatives with electron-donating substituents than is the case for the cyclopropylmethyl cation intermediate. Thus the solvolysis reaction proceeds via two independent pathways: one has a cyclopropyl cation intermediate and the other has a homoallylic cation intermediate.

Due to the high degree of p-orbital character of C–C bonds relative to the saturated C–C bonds,[2)] a cyclopropane ring is able to stabilize the adjacent charge to a greater extent than alkyl groups do.[3)] It is well known that the cyclopropylmethyl derivatives solvolyse extraordinarily faster than the alkyl derivatives and afforded a variety of reaction products.[3,4)] The cyclopropylmethyl cation has a bisected conformation where C–C bonds of cyclopropyl group achieve the maximum overlap with the vacant p-orbital of the cationic center and the positive charge develops at 2-position of the cyclopropyl group (Chart 1),[3)] Schleyer and Dine reported the solvolysis rates of the 2-substituted cyclopropylmethyl 3,5-dinitrobenzoates: the 2-methyl derivative solvolysed about 10 times faster than the parent compound.[5)] The substituents in their study, however, were limited to the alkyl and ethoxy groups. Shono and co-workers examined the solvolyses of 2-arylcyclopropylmethyl 3,5-dinitrobenzoates.[6)] While the reactivity was correlated by σ^+ values, the substituents measured were limited to those at the *para* position and the number was only 4. It appeared that more experimental data would be helpful to clarify the substituent effect at the 2-position of the cyclopropyl group and the reaction mechanism of the solvolysis of cyclopropylmethyl derivatives, since the reaction process may change depending on the electron-donating ability of the substituent. In this paper, the solvolysis rates and the reaction products of 1-[*trans*-2-(*m*- or *p*-substituted phenyl)cyclopropyl]-1-methylethyl *p*-nitrobenzoates **1** will be examined as a continuation of the study concerning the reactivity of the molecules including the cyclopropane ring (Chart 2).[7,8)]

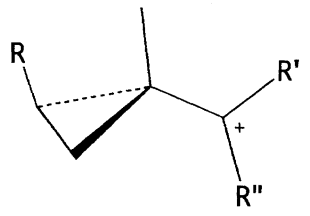
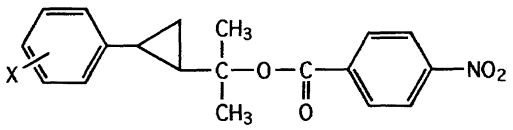


Chart 1.

Results and Discussion

The solvolysis rates of **1** in 80% aqueous acetone were determined by conductmetric measurements at the initial concentrations of 10^{-3}—10^{-5} mol dm^{-3}. The reaction showed linear first-order kinetics over 70% reaction. The reproducibilities of the rate constants were within an accuracy of 3%. The obtained rate constants and the activation parameters at 45 °C are summarized in Table 1. The products of the hydrolysis of **1f** were investigated by high performance liquid chromatographic techniques and NMR. The identified products were 2-(*trans*-2-phenylcyclopropyl)-2-propanol (**2f**) 85%, 4-methyl-1-phenyl-3-penten-1-ol (**3f**) 9%, and 4-methyl-1-phenyl-3-pentenyl *p*-nitrobenzoate (**4f**) 4.9% (Chart 3). For all benzoates **1**, the product analyses were conducted by ^{1}H NMR spectra (400 MHz) in 20% deuterium



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1a: X=*p*-CH_3O, **1b**: X=*p*-C_2H_5O, **1c**: X=*p*-CH_3, **1d**: X=*p*-C_2H_5, **1e**: X=*p*-*t*-C_4H_9, **1f**: X=H, **1g**: X=*p*-F, **1h**: X=*p*-Cl, **1i**: X=*p*-Br, **1j**: X=*m*-CH_3, **1k**: X=*m*-CH_3O, **1l**: X=*m*-Cl, **1m**: X=*m*-Br, **1n**: X=*m*-CF_3

Chart 2.

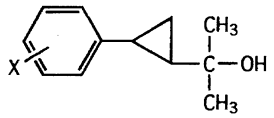
Table 1. Solvolysis Rates and Activation Parameters for 1-[*trans*-2-(*m*- or *p*-Substituted Phenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoates in 80 : 20 Acetone–Water

Subst.	Temp	10^5k	$\Delta H^{\ddagger}_{45\,°C}$ [a)]	$\Delta S^{\ddagger}_{45\,°C}$ [a)]
	°C	s^{-1}	kcal mol^{-1}	e.u.
H	25	1.50		
	35	5.07		
	45	17.6	22.5	−5.03
p-CH_3O	25	7.12		
	35	25.3		
	45	84.0	22.6	−1.7
p-C_2H_5O	25	7.30		
	35	24.9		
	45	73.7	21.2	−6.5
p-CH_3	25	3.03		
	35	10.6		
	45	32.0	21.7	−6.3
p-C_2H_5	25	2.80		
	35	9.03		
	45	30.9	22.0	−5.7
p-*t*-C_4H_9	35	2.38		
	45	28.5	22.2	−5.2
	55	86.7		
p-F	35	4.31		
	45	14.0	22.7	−5.0
	55	44.0		
p-Cl	25	0.621		
	35	2.38		
	45	7.63	23.0	−5.2
p-Br	25	0.604		
	35	2.08		
	45	7.23	22.7	−6.2
m-CH_3	35	6.02		
	45	20.6	22.0	−6.5
	55	57.2		
m-CH_3O	35	4.08		
	45	13.8	23.0	−4.1
	55	42.9		
m-Cl	35	1.36		
	45	4.26	21.9	−9.7
	55	12.9		
m-Br	45	4.59	20.1	−15.3
	55	12.4		
	65	32.0		
m-CF_3	35	0.896		
	45	2.86	22.4	−8.9
	55	8.92		

a) 1 cal = 4.184 J.

oxide-80% acetone-d_6 within the temperature range of the kinetic study. The integrated peaks used for determination of product ratio were at $\delta = 0.82$—0.83 for **2**, $\delta = 2.8$—3.0 for **3**, and $\delta = 3.0$—3.2 for **4**, respectively. The distributions of the products thus obtained were little affected by reaction time or by added 2,6-lutidine or pyridine. The results are listed in Table 2.

The product distribution data reveal a distinct difference between the two alkoxy groups and the less reactive groups (*m*-Cl, *m*-Br, and *m*-CF_3). The product of *m*-Br derivative (**1m**) was only the corresponding 2-(2-arylcyclopropyl)-2-propanol, **2m**. The ring-opened products (**3**, **4**) increased as the electron-donating ability of the substituent increased. For *p*-methyl derivative (**1c**) the ratio of **2c/3c** is 1. For the two alkoxy derivatives (**1a** and **1b**), however, the main product (> 75%) is the ring-opened product (**3a** or **3b**) and the amount of the parent substituted 2-propanol (**2a** or **2b**) is only 4%.



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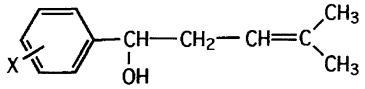

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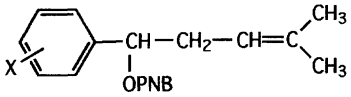

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Chart 3.

Table 2. Products Distributions in the Solvolysis of 1-[*trans*-2-(*m*- or *p*-Substituted Phenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoates in 80% Aqueous Acetone

Subst.	**2**	**3**	**4**	Unidentified products
H	85	9	5	1
p-CH_3O	2	75	22	1
p-C_2H_5O	4	85	10	1
p-CH_3	41	41	17	1
p-C_2H_5	53	39	8	0
p-*t*-C_4H_9	47	34	15	5
p-F	78	14	7	1
p-Cl	92	4	2	2
p-Br	93	4	3	0
m-CH_3	76	17	7	0
m-Cl	98	1	1	0
m-Br	100			
m-CF_3	97	1	1	1

The relative reactivities obtained are illustrated in Fig. 1. Here the log (k/k_0) values were plotted against for σ^0 values for *p*-substituted derivatives and for σ_m values for *m*-substituted derivatives.[9—11] An excellent correlation was obtained with a slope (ρ_m) of −1.49 with a correlation coefficient of 0.998 and with a standard deviation of 0.026 for the *m*-substituted derivatives. The negative value of ρ_m indicates that the positive charge is delocalized to some extent to the 2-

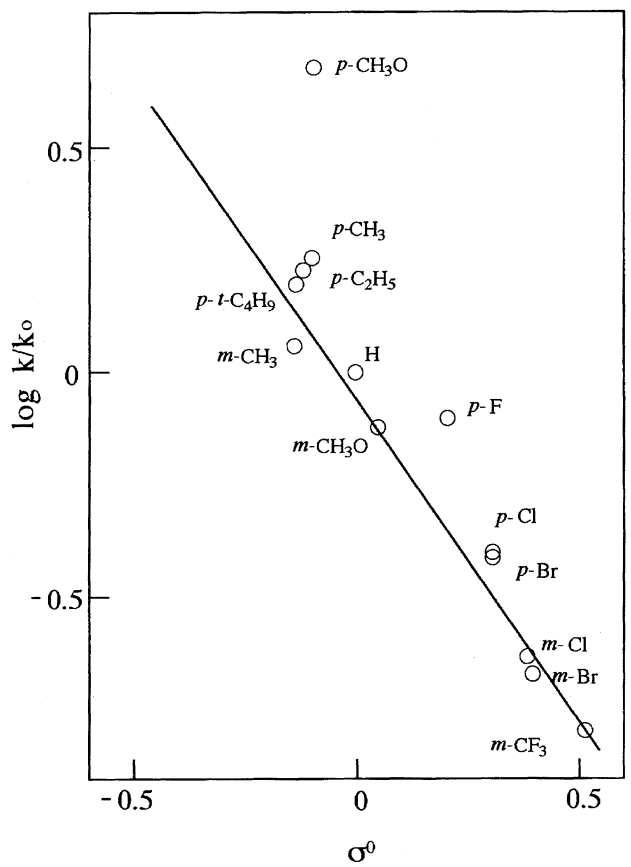


Fig. 1. Variations of reactivity with the σ^0 values for the solvolysis of 1-[*trans*-2-(*m*- or *p*-substituted phenyl)cyclopropyl]-1-methylethyl *p*-nitrobenzoates in 80% aqueous acetone.

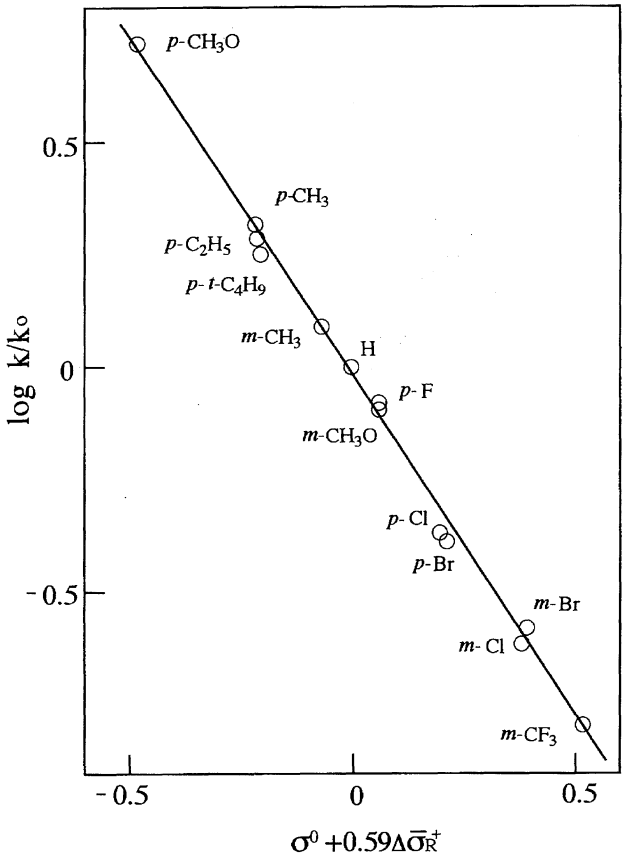


Fig. 2. Application of Eq. 1 to the solvolysis of 1-[*trans*-2-(*m*- or *p*-substituted phenyl)cyclopropyl-1-methylethyl *p*-nitrobenzoates.

position of the cyclopropyl group, while the absolute value (1.49) is much smaller than that (4.95) determined from the solvolysis of 1-aryl-1-methylethyl chlorides[12,13] and those from the solvolyses of the other benzylic derivatives.[14—17] It is noticeable that the *p*-derivatives deviate remarkably upward from the regression line determined by the *m*-substituted derivatives, due to the considerable contribution of the exalted resonance effect at the intermediate in the present solvolysis.

It is well established that the resonance effect of the substituents may be evaluated strictly in terms of the following linear free-energy relationship (Y–T equation or LArSR equation)[18—20] presented by Yukawa and Tsuno:

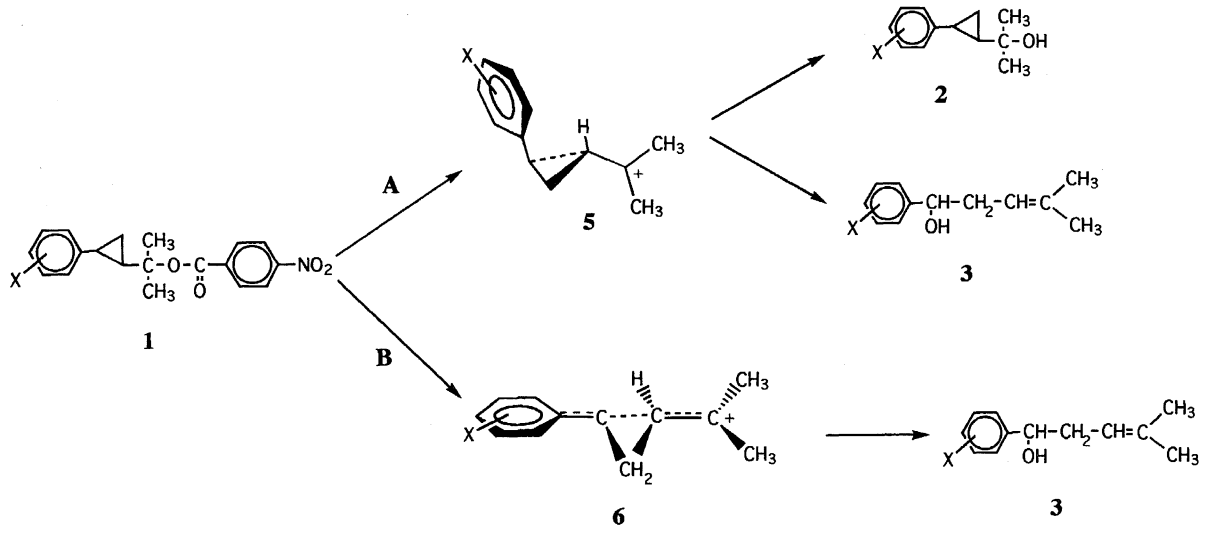
$$\log(k/k_0) = \rho(\sigma^0 + r\Delta\overline{\sigma}_R^+), \quad (1)$$

where r is a constant depending on the resonance requirement of the reaction and where $\Delta\overline{\sigma}_R^+$ measures the capacities of the substituents to supply electrons by resonance. The application of this equation to the solvolysis reactivity of **1** gave a good correlation, with a correlation coefficient of 0.997 and a standard deviation of 0.04,[21] as is graphed in Fig. 2.

$$\log(k/k_0) = -1.43(\sigma^0 + 0.59\Delta\overline{\sigma}_R^+) - 0.06. \quad (2)$$

The r value thus obtained is near to that for the solvolysis of 3′- and 4′-substituted 1-(4-biphenylyl)-1-methylethyl chlorides in 90% aqueous acetone (r=0.67 and ρ=−1.39).[16,17,22] The r value (0.59) is considered to be an extraordinarily large one since *trans*-1,2-cyclopropanediyl group is a poor transmitter of the resonance effect.[3,8,23] The transmitting resonance effect of *trans*-1,2-cyclopropanediyl group in the solvolyses of $ArCHClCH_3$ in 80% aqueous acetone is a third of *p*-phenylene group as evaluated by Yukawa–Tsuno (LSFE) equation.[8] Moreover, the CNDO calculation for 2-substituted cyclopropylmethyl cations showed that the LUMO of the cations had a small coefficient at C_2, so the interactions at this position are small.[24]

It is inferred that the large r value here obtained arises not only from the resonance contribution of the *p*-substituent in the cyclopropyl-substituted carbenium ion intermediate (**5**) but also from the resonance contribution of *p*-substituent in the other intermediate, homoallylic cation (**6**)[25] where much positive charge develops at the benzylic carbon. Thus, the solvolyses of **1** proceed through the two different reaction pathways competitively, as speculated in Scheme 1. Solvolyses of the less reactive derivatives (**1l**, **1m**, and **1n**) proceed via the process A and form exclusively the parent alcohol as the product. The solvolysis of **1** is favorable to the process B when the substituent is electronically releasing. There occurs the changeover of the reaction process depending on the electron-donating ability of the substituents on the ben-



Scheme 1.

zene ring. The *p*-methoxy and the *p*-ethoxy groups stabilize strongly the benzylic cation center by resonance. Hence, **1a** and **1b** solvolyze mainly through the process B to give predominantly the ring-opened product **3**. It appears, however, that **2a** (<5%) or **2b** were formed by process A. It is unclear how **4** forms.

Experimental

All melting points were measured on a hot-stage melting-point apparatus and were uncorrected. Solvents were predried with a molecular sieve and were freshly distilled before use. Solutions were evaporated under reduced pressure and/or chromatographed on a silica-gel column using an ethyl acetate–hexane mixture as the eluent. Boiling points were uncorrected. HPLC were performed with a JASCO TRIROTOR-V using a Finepack SIL column with a Shodex RI SE-51 detector. Preparative scale LC separations were carried out on a Shodex LC PR 100, packed with a Merck Lichroprep Si 60 gel. Unless otherwise stated, NMR spectra were determined as a solution in $CDCl_3$ (90 MHz for ^1H and 22.4 MHz for ^{13}C, JEOL EX 90 spectrometer). Chemical shifts are reported in δ units downfield from internal $(CH_3)_4Si$. Analyses of solvolysis products were carried out by ^1H NMR (400 MHz, JEOL Lambda 400 spectrometer).

Ethyl 2-(substituted phenyl)-1-cyclopropanecarboxylates were prepared by the reaction of the corresponding substituted styrenes with ethyl diazoacetate in the presence of palladium(II) acetate.[26] The geometrical isomers were conveniently separated by HPLC. The identification of the geometrical isomers of substituted cyclopropanes were made by the ^{13}C NMR spectra, where the *cis* isomers always resonated at higher field than the corresponding *trans* isomers did.[27,28] All the 2-[*trans*-2-(substituted phenyl)cyclopropyl]-2-propanols were prepared by the reaction of the corresponding ethyl *trans*-2-(substituted phenyl)-1-cyclopropanecarboxylates with methylmagnesium bromide in ether. All the 1-[*trans*-2-(substituted phenyl)cyclopropyl]-1-methylethyl *p*-nitrobenzoates were obtained by the reaction of the corresponding substituted 2-propanols with *p*-nitrobenzoyl chloride in the presence of pyridine in 15—20% yields. The *p*-nitrobenzoates were purified carefully by the recrystallization from hexane–benzene mixtures before the kinetic measurements.

2-(*trans*-2-Phenylcyclopropyl)-2-propanol (2f): To 7 ml of ether solution of methylmagnesium bromide (3 mol dm^{-1}) purchased from TCI was added dropwise 0.95 g of ethyl *trans*-2-phenyl-1-cyclopropanecarboxylate in 15 ml of ether under argon atmosphere. The mixture was stirred at room temperature for 2 h. A dilute aqueous ammonium chloride solution was added slowly. The ether layer was separated and the aqueous layer was extracted with ether. The combined etherial solution was dried over anhydrous magnesium sulfate, and ether was removed under reduced pressure, (5 mmHg, 1 mmHg=133.322 Pa).[29] The obtained material was purified by HPLC. Colorless oil; ^1H NMR δ=0.70—1.35 (3H, m), 1.25 (6H, s), 1.75 (1H, s), 1.85—2.10 (1H, m), 7.00—7.35 (5H, m); ^{13}C NMR δ=11.67 (CH_2), 19.20 (CH), 28.94 (CH_3), 29.05 (CH_3), 34.09 (CH), 69.35, 125.98 (CH), 128.25 (CH), 143.26.

2-[*trans*-2-(*p*-Tolyl)cyclopropyl]-2-propanol (2c): Colorless oil; ^1H NMR δ=0.65—1.20 (3H, m), 1.25 (6H, s), 1.60—2.15 (2H, m), 2.25 (3H, s), 6.80—7.35 (5H, m); ^{13}C NMR δ=11.47 (CH_2), 18.90 (CH), 20.92 (CH_3), 28.92 (CH_3), 29.12 (CH_3), 33.91 (CH), 69.48, 125.96 (CH), 128.99 (CH), 134.94, 140.14.

2-[*trans*-2-(*p*-Ethylphenyl)cyclopropyl]-2-propanol (2d): Colorless oil; ^1H NMR δ=0.50—1.75 (13H, m), 1.75—2.05 (1H, m), 2.60 (2H, q, J=7.1 Hz), 6.85—7.25 (5H, m); ^{13}C NMR δ=11.52 (CH_2), 15.63 (CH_3), 18.90 (CH), 28.39 (CH_2), 28.93 (CH_2), 29.11 (CH_3), 33.88 (CH), 69.38, 125.99 (CH), 127.76 (CH), 140.43, 141.34.

2-[*trans*-2-(*p*-*t*-Butylphenyl)cyclopropyl]-2-propanol (2e): Colorless oil; ^1H NMR δ=0.65—1.2 (3H, m), 1.20 (6H, s), 1.25 (9H, s), 1.45—1.65 (1H, m), 1.65—2.05 (1H, m), 7.00 (2H, d, J=9 Hz), 7.30 (2H, d, J=9 Hz); ^{13}C NMR δ=11.61 (CH_2), 18.79 (CH), 28.95 (CH_3), 29.13 (CH_3), 31.40 (CH_3, three carbons), 33.79 (CH), 34.30, 69.44 (C–O), 125.17 (CH), 125.69 (CH), 140.15, 148.29.

2-[*trans*-2-(*p*-Fluorophenyl)cyclopropyl]-2-propanol (2g): Colorless oil; ^1H NMR δ=0.60—0.85 (1H, m), 0.90—1.45 (2H, m), 1.25 (6H, s), 1.85—2.15 (2H, m), 6.80—7.15 (4H, m); ^{13}C NMR δ=11.46 (CH_2), 18.52 (CH), 29.02 (CH_3, two carbons), 33.98 (CH), 69.25 (C–O), 114.99 (d, J=21.4 Hz), 127.53 (d, J=7.63 Hz), 138.90, 161.11 (d, J=242.92 Hz).

2-[*trans*-2-(*p*-Chlorophenyl)cyclopropyl]-2-propanol (2h): Mp 49 °C; ^1H NMR δ=0.55—1.55 (4H, m), 1.25 (6H, s), 1.75—2.05 (1H, m), 6.98 (2H, d, J=8.54 Hz), 7.20 (2H, d, J=8.55 Hz); ^{13}C NMR δ=11.76 (CH_2), 18.69 (CH), 29.07 (CH_3), 29.13 (CH_3), 34.27 (CH), 69.26 (C–O), 127.36 (CH), 127.60 (CH), 131.01, 141.86.

2-[*trans*-2-(*p*-Bromophenyl)cyclopropyl]-2-propanol (2i): Colorless oil; ^1H NMR δ=0.60—1.50 (4H, m), 1.25 (6H, s), 1.75—

2.00 (1H, m), 6.87 (2H, d, J=8.5 Hz), 7.30 (2H, d, J=8.5 Hz); ^{13}C NMR δ=11.73 (CH_2), 18.70 (CH), 29.06 (CH_3, two carbons), 34.29 (CH), 69.08, 118.84, 127.93 (CH), 131.21 (CH), 142.43.

2-[*trans*-2-(*p*-Methoxyphenyl)cyclopropyl]-2-propanol(2a): Colorless oil; ^{1}H NMR δ=0.70—1.75 (4H, m), 1.27 (6H, s), 1.85—2.15 (1H, m), 3.76 (3H, s), 6.90 (2H, d, J=8.5 Hz), 7.15 (2H, d, J=8.4 Hz); ^{13}C NMR δ=11.11 (CH_2), 18.52 (CH), 28.95 (CH_3), 29.08 (CH_3), 33.60 (CH), 55.28 (CH_3), 69.32, 113.93 (CH), 127.21 (CH), 135.34, 157.76.

2-[*trans*-2-(*p*-Ethoxyphenyl)cyclopropyl]-2-propanol (2b): Colorless oil; ^{1}H NMR δ=0.65—1.25 (3H, m), 1.25 (6H, s), 1.35 (3H, t, J=7 Hz), 1.65 (1H, s), 1.75—1.00 (1H, m), 3.95 (2H, q, J=7 Hz), 6.75 (2H, d, J=9 Hz), 6.95 (2H, d, J=9 Hz); ^{13}C NMR δ=11.13 (CH_2), 14.86 (CH_3), 18.50 (CH), 28.92 (CH_3), 29.06 (CH_3), 33.56 (CH), 63.49 (CH_2), 69.33 (C–O), 114.53 (CH), 127.13 (CH), 135.14, 157.01.

2-[*trans*-2-(*m*-Tolyl)cyclopropyl]-2-propanol (2j): Colorless oil; ^{1}H NMR δ=0.60—1.35 (3H, m), 1.25 (6H, s), 1.53 (1H, s), 1.75—2.00 (1H, m), 2.29 (3H, s), 6.75—7.20 (3H, m), 7.32 (1H, s); ^{13}C NMR δ=11.61 (CH_2), 19.16 (CH), 21.36 (CH_3), 28.95 (CH_3), 29.06 (CH_3), 34.01 (CH), 69.36 (C–O), 123.03 (CH), 126.22 (CH), 126.80 (CH), 128.20 (CH), 137.74, 143.22.

2-[*trans*-2-(*m*-Methoxyphenyl)cyclopropyl]-2-propanol (2k): Colorless oil; ^{1}H NMR δ=0.65—1.55 (3H, m), 1.25 (6H, s), 1.66 (1H, s), 1.75—2.05 (1H, m), 3.74 (3H, s), 6.6—6.75 (2H, m), 7.0—7.4 (2H, m); ^{13}C NMR δ=11.69 (CH_2), 19.31 (CH), 28.99 (CH_3), 29.10 (CH_3), 34.14 (CH), 55.07 (CH_3), 69.25, 110.72 (CH), 112.05 (CH), 118.49 (CH), 129.24 (CH), 145.11, 159.74.

2-[*trans*-2-(*m*-Chlorophenyl)cyclopropyl]-2-propanol (2l): Colorless oil; ^{1}H NMR δ=0.65—1.60 (3H, m), 1.25 (6H, s), 1.75 (1H, s), 1.80—2.05 (1H, m), 6.80—7.15 (3H, m), 7.30 (1H, s); ^{13}C NMR δ=11.84 (CH_2), 18.90 (CH), 29.03 (CH_3), 29.05 (CH_3), 34.37 (CH), 69.17, 124.27 (CH), 125.48 (CH), 126.02 (CH), 129.45 (CH), 134.09, 145.60.

2-[*trans*-2-(*m*-Bromophenyl)cyclopropyl]-2-propanol (2m): Colorless oil; ^{1}H NMR δ=0.70—1.40 (3H, m), 1.26 (6H, s), 1.57 (1H, s), 1.75—2.05 (1H, m), 6.95—7.35 (4H, m); ^{13}C NMR δ=11.77 (CH_2), 18.80 (CH), 28.98 (CH_3, two carbons), 34.25 (CH), 122.35, 124.66 (CH), 128.35 (CH), 128.90 (CH), 129.65 (CH), 145.76.

2-[*trans*-2-(*m*-Trifluoromethylphenyl)cyclopropyl]-2-propanol (2n): Colorless oil; ^{1}H NMR δ=0.70—1.25 (3H, m), 1.29 (6H, s), 1.40—1.70 (1H, m), 1.85—2.15 (1H, m), 7.15—7.40 (4H, m); ^{13}C NMR (100 MHz) δ=12.05 (CH_2), 19.08 (CH), 29.21 (CH_3, two carbons), 34.51 (CH), 69.26 (C–O), 122.26 (CH), 122.63 (CH), 124.28 (q, J_{CF}=270.5 Hz), 128.68 (CH), 129.41 (CH), 130.69 (q, $^2J_{CF}$=31.8 Hz).

1-(*trans*-2-Phenylcyclopropyl)-1-methylethyl *p*-Nitrobenzoate (1f): To 0.88 g (0.005 mol) of 2-(*trans*-2-phenylcyclopropyl)-2-propanol in 10 ml of pyridine was added 0.97 g (0.0053 mol) of *p*-nitrobenzoyl chloride with stirring. The mixture was allowed to stand overnight at room temperature. 20 ml of benzene and then 15 ml of water was added; the benzene layer was separated and washed with diluted hydrochloric acid and water to remove pyridine. The solution was dried over anhydrous magnesium sulfate and benzene was removed under reduced pressure (4 mmHg).[29] The obtained *p*-nitrobenzoate was purified by recrystallization from the hexane–benzene mixture. 0.40 g (23%); Mp 95—96 °C; Anal. Found: C, 70.05; H, 5.90; N, 4.25%. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31%. ^{1}H NMR δ=1.90—1.40 (2H, m), 1.65 (6H, s), 1.70—2.0 (1H, m), 2.0—2.3 (1H, m), 7.0—7.5 (5H, m), 8.10 (2H, d, J=8.5 Hz), 8.25 (2H, d, J=8.5 Hz); ^{13}C NMR δ=12.23 (CH_2), 20.29 (CH), 25.08 (CH_3), 32.11 (CH), 83.90, 123.46 (CH), 123.89 (CH, *p*-), 126.23 (CH), 128.41 (CH), 130.49 (CH), 137.41, 142.16, 150.36, 163.49.

1-[*trans*-2-(*p*-Tolyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1c). Mp 85 °C; ^{1}H NMR δ=0.95—1.05 (1H, m), 1.14—1.24 (1H, m), 1.57 (1H, bs), 1.63 (3H, s), 1.64 (3H, s), 1.64—1.77 (1H, m), 2.09—2.18 (1H, m), 2.31 (3H, s), 7.01 (2H, d, J=8.1 Hz), 7.08 (2H, d, J=8.1 Hz), 8.12 (2H, d, J=8.6 Hz), 8.26 (2H, d, J=8.6 Hz); ^{13}C NMR (100 MHz) δ=12.10 (CH_2), 19.90 (CH), 20.10 (CH_3), 25.06 (CH_3, two carbons), 31.94 (CH), 83.98 (C–O), 123.44 (CH), 126.11, 129.09 (CH), 130.48 (CH), 135.41, 137.40, 139.08, 150.58, 163.49 (C=O). Anal. Found: C, 70.11; H, 6.24; N, 4.08%. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13%.

1-[*trans*-2-(*p*-Ethylphenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1d): Mp 61 °C; ^{1}H NMR δ=0.85—1.35 (2H, m), 1.21 (3H, t, J=7.6 Hz), 1.55—1.95 (1H, m), 1.64 (6H, s), 1.95—2.25 (1H, m), 2.62 (2H, q, J=8.5 Hz), 7.0—7.20 (4H, bs), 8.10 (2H, d, J=9.0 Hz), 8.27 (2H, d, J=9.2 Hz); ^{13}C NMR δ=12.11 (CH_2), 15.58 (CH_3), 19.96 (CH), 25.07 (CH_3, two carbons), 28.41 (CH_2), 31.86 (CH), 83.99, 123.45 (CH), 126.22 (CH), 127.90 (CH), 130.50 (CH), 137.44, 139.33, 141.86, 150.34, 163.49. Anal. Found: C, 70.82; H, 6.53; N, 3.93%. Calcd for $C_{21}H_{23}NO_4$: C, 71.37; H, 6.56; N, 3.96%.

1-[*trans*-2-(*p*-*t*-Butylphenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1e): Mp 123.5 °C; ^{1}H NMR δ=0.80—1.30 (2H, m), 1.30 (6H, s), 1.50—1.90 (1H, m), 1.64 (6H, s), 1.90—2.25 (1H, m), 7.05 (2H, d, J=8.5 Hz), 7.30 (2H, d, J=8.5 Hz), 8.15 (2H, d, J=8.7 Hz), 8.25 (2H, d, J=8.6 Hz); ^{13}C NMR δ=12.11 (CH_2), 19.88 (CH), 25.05 (CH_3), 25.17 (CH_3), 31.41 (CH_3), 31.74 (CH), 34.38 (CH), 84.03 (C–O), 123.45 (CH), 125.31 (CH), 126.00, 130.50 (CH), 137.49, 139.07, 148.83, 150.41, 163.55. Anal. Found: C, 72.12; H, 7.23; N, 3.86%. Calcd for $C_{23}H_{27}NO_4$: C, 72.42; H, 7.13; N, 3.67%.

1-[*trans*-2-(*p*-Fluorophenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1g): Mp 111 °C; ^{1}H NMR (400 MHz with ^{19}F decoupling) δ=0.95—1.01 (1H, m), 1.16—1.22 (1H, m), 1.56 (1H, s), 1.64 (6H, s), 1.67—1.74 (1H, m), 2.02—2.25 (1H, m), 6.95 (2H, d, J=8.8 Hz), 7.07 (2H, d, J=8.5 Hz), 8.12 (2H, d, J=8.8 Hz), 8.27 (2H, d, J=9.0 Hz); ^{13}C NMR δ=12.08 (CH_2), 19.68 (CH), 24.90 (CH_3), 25.25 (CH_3), 31.91 (CH), 83.86 (C–O), 115.16 (d, $^2J_{CF}$=21.36 Hz), 123.45 (CH), 127.79 (d, $^3J_{CF}$=7.93 Hz), 130.47 (CH), 137.38, 137.69, 150.42, 161.35 (d, J_{CF}=243.83 Hz), 163.52 (C=O). Anal. Found: C, 67.46; H, 5.77; N, 3.96%. Calcd for $C_{19}H_{18}FNO_4$: C, 66.44; H, 5.29; N, 4.08%.

1-[*trans*-2-(*p*-Chlorophenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1h): Mp 97 °C; ^{1}H NMR δ=0.80—1.20 (2H, m), 1.3—1.8 (1H, m), 1.55 (6H, s), 1.80—2.20 (1H, m), 6.90 (2H, d, J=8.5 Hz), 7.15 (2H, d, J=8.4 Hz), 8.00 (2H, d, J=8.6 Hz), 8.15 (2H, d, J=8.6 Hz); ^{13}C NMR δ=12.35 (CH_2), 19.85 (CH), 24.86 (CH_3), 25.29 (CH_3), 32.21 (CH), 83.76 (C–O), 123.46 (CH), 127.61 (CH), 128.51 (CH), 130.47 (CH), 131.60, 137.32, 140.70, 150.45, 163.51. Anal. Found: C, 63.83; H, 5.24; N, 3.82%. Calcd for $C_{19}H_{18}ClNO_4$: C, 63.4; H, 5.04; N, 3.89%.

1-[*trans*-2-(*p*-Bromophenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1i): Mp 87 °C; ^{1}H NMR δ=0.85—1.30 (2H, m), 1.64 (6H, s), 1.5—1.9 (1H, m), 1.9—2.25 (1H, m), 6.95 (2H, d, J=8 Hz), 7.35 (2H, d, J=8 Hz), 8.1 (2H, d, J=8.5 Hz), 8.25 (2H, d, J=8.5 Hz); ^{13}C NMR δ=12.38 (CH_2), 19.92 (CH), 24.86 (CH_3), 25.30 (CH_3), 32.23 (CH), 83.75, 119.50, 123.48 (CH), 127.99 (CH), 130.47 (CH), 131.46 (CH), 137.32, 141.27, 150.49, 163.53. Anal. Found: C, 56.49; H, 4.47; N, 3.48%. Calcd for $C_{19}H_{18}BrNO_4$: C, 56.45; H, 4.49; N, 3.46%.

1-[*trans*-2-(*p*-Methoxyphenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1a): Mp 106 °C; ^{1}H NMR δ=0.85—1.4 (2H, m), 1.4—1.8 (1H, m), 1.64 (6H, s), 1.9—2.2 (1H, m), 3.78 (3H, s), 6.80 (2H, d, J=8 Hz), 7.05 (2H, d, J=8 Hz), 8.10 (2H, d, J=8.5 Hz), 8.25 (2H, d, J=8.5 Hz); ^{13}C NMR δ=11.68 (CH_2), 19.51 (CH), 24.95 (CH_3), 31.54 (CH), 55.24 (CH_3), 84.00, 113.89 (CH), 123.36 (CH), 127.35 (CH), 130.40 (CH), 134.06, 137.47, 150.36, 157.97, 163.50. Anal. Found: C, 66.90; H, 5.85; N, 4.06%. Calcd for $C_{20}H_{21}NO_5$: C, 67.59; H, 5.96; N, 3.94%.

1-[*trans*-2-(*p*-Ethoxyphenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1b): Mp 79 °C; ^{1}H NMR δ=0.85—1.25 (2H, m), 1.35 (3H, t, J=7 Hz), 1.65 (6H, s), 1.5—1.85 (1H, m) 1.85—2.35 (1H, m), 3.95 (2H, q, J=7 Hz), 6.75 (2H, d, J=8 Hz), 7.0 (2H, d, J=8 Hz), 8.05 (2H, d, J=8.5 Hz), 8.25 (2H, d, J=8.5 Hz); ^{13}C NMR δ=11.77 (CH_2), 14.89 (CH_3), 19.60 (CH), 25.05 (CH_3), 25.14 (CH_3), 31.61 (CH), 63.54 (CH_2), 84.09 (C–O), 114.58 (CH), 123.44 (CH), 127.40 (CH), 130.49 (CH), 134.00, 137.50, 150.39, 157.38, 163.53. Anal. Found: C, 68.46; H, 6.32; N, 3.82%. Calcd for $C_{21}H_{23}NO_5$: C, 68.28; H, 6.28; N, 3.79%.

1-[*trans*-2-(*m*-Methylphenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1j): Mp 89 °C; ^{1}H NMR δ=0.85—1.30 (2H, m), 1.6—1.2 (1H, m), 1.65 (6H, s), 1.95—2.2 (1H, m), 2.31 (3H, s), 6.8—7.25 (4H, m), 8.10 (2H, d, J=8.5 Hz), 8.25 (2H, d, J=8.5 Hz); ^{13}C NMR δ=12.18 (CH_2), 20.25 (CH), 21.40 (CH_3), 25.05 (CH_3), 25.13 (CH_3) 32.06 (CH), 83.99, 123.27 (CH), 123.44 (CH, two carbons), 126.68 (CH), 126.98 (CH), 128.33 (CH), 130.49 (CH, two carbons), 137.47, 137.99, 142.12, 150.41, 163.52 (C=O). Anal. Found: C, 70.92; H, 6.21; N, 4.16%. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13%.

1-[*trans*-2-(*m*-Methoxyphenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1k): Mp 118 °C; ^{1}H NMR δ=0.9—1.4 (2H, m), 1.5—1.95 (1H, m), 1.64 (6H, s), 1.95—2.30 (1H, m), 3.78 (3H, s), 6.6—6.8 (2H, m), 7.05—7.4 (2H, m), 8.05 (2H, d, J=8.5 Hz), 8.35 (2H, d, J=8.5 Hz); ^{13}C NMR δ=12.25 (CH_2), 20.36 (CH), 25.02 (CH_3), 25.12 (CH_3), 32.16 (CH), 55.17 (CH_3), 83.88, 111.10 (CH), 112.28 (CH), 118.66 (CH), 123.45 (CH), 129.39 (CH), 130.49, 143.92, 137.41, 150.39, 159.82, 163.50. HRMS Found: m/z 355.1436. Calcd for $C_{20}H_{21}NO_5$: M, 355.1420. Anal. Found: C, 67.66; H, 5.99; N, 3.54%. Calcd for $C_{20}H_{21}NO_5$: C, 67.57; H, 5.69; N, 3.94%.

1-[*trans*-2-(*m*-Chlorophenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1l): Mp 102 °C; ^{1}H NMR δ=0.85—1.30 (2H, m), 1.57 (6H, s), 1.6—1.9 (1H, m), 1.95—2.25 (1H, m), 6.9—7.3 (4H, m), 8.05 (2H, d, J=8.5 Hz), 8.35 (2H, d, J=8.5 Hz); ^{13}C NMR δ=12.44 (CH_2), 20.06 (CH), 24.87 (CH_3), 25.22 (CH_3), 32.40 (CH), 83.63, 123.48 (CH), 124.46 (CH), 126.04 (CH), 126.34 (CH), 129.62 (CH), 130.48 (CH), 134.32, 137.25, 144.37, 150.39, 163.47. Anal. Found: C, 62.88; H, 4.97; N, 3.88%. Calcd for $C_{19}H_{18}ClNO_4$: C, 63.43; H, 5.04; N, 3.89%.

1-[*trans*-2-(*m*-Bromophenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1m): Mp 77 °C; ^{1}H NMR δ=0.8—1.3 (2H, m), 1.6—1.9 (1H, m), 1.64 (6H, s), 1.95—2.25 (1H, m), 7.0—7.35 (4H, m), 8.10 (2H, d, J=8.1 Hz), 8.25 (2H, d, J=8.5 Hz); ^{13}C NMR δ=12.42 (CH_2), 20.06 (CH), 24.86 (CH_3), 25.28 (CH_3), 32.41 (CH), 83.67, 122.61 (C–Br), 123.49 (CH), 124.94 (CH), 129.01 (CH), 129.38 (CH), 129.93 (CH), 130.49 (CH), 137.30, 144.67, 150.46, 163.49. Anal. Found: C, 56.56; H, 4.41; N, 3.28%. Calcd for $C_{19}H_{18}BrNO_4$: C, 56.45; H, 4.49; N, 3.47%.

1-[*trans*-2-(*m*-Trifluoromethylphenyl)cyclopropyl]-1-methylethyl *p*-Nitrobenzoate (1n): Mp 81 °C; ^{1}H NMR δ=1.01—1.40 (2H, m), 1.65 (6H, s), 1.7—1.95 (1H, m), 2.1—2.35 (1H, m), 7.20—7.50 (4H, m), 8.10 (2H, d, J=8.5 Hz), 8.25 (2H, d, J=8.5 Hz); ^{13}C NMR (100 MHz) δ=12.47 (CH_2), 20.17 (CH), 24.73 (CH_3), 25.34 (CH_3), 32.47 (CH), 83.61, 122.70 (CH, q, $^3J_{CF}$=3.73 Hz), 123.07 (CH, q, $^3J_{CF}$=3.73 Hz), 123.49 (CH), 124.18 (CF_3, q, J_{CF}=271.7 Hz), 128.84 (CH), 129.50 (CH), 130.47 (CH), 130.77 (q, $^2J_{CF}$=33.1 Hz), 137.19, 143.19, 150.38, 163.49. Anal. Found: C, 61.30; H, 4.59; N, 3.54%. Calcd for $C_{19}H_{18}F_3NO_4$: C, 61.10; H, 4.61; N, 3.56%.

Product Studies: A solution of 0.1 g of 1-(*trans*-2-phenylcyclopropyl)-1-methylethyl *p*-nitrobenzoate and 0.2 g of pyridine (or 2, 4-lutidine) in 25 ml of 80% aqueous acetone was allowed to remain at 30 °C for several half-lives. The solution was diluted with water and extracted with benzene. The benzene solution was washed with dilute hydrochloric acid and water, and dried with anhydrous magnesium sulfate. The relative amounts of the products were determined by ^{1}H NMR (400 MHz) at acetone-d_6 solution. The main products were separated by HPLC and confirmed by ^{13}C NMR and the Mass spectra. The relative amounts of the products for other derivatives were determined in a solution of 0.005 g of the *p*-nitrobenzoates in 2 ml of acetone-d_6-deuterium oxide (4 : 1) directly by ^{1}H NMR (400 MHz).

Kinetic Measurements: 80% aqueous acetone was prepared by mixing the corresponding volumes of two components at room temperature. The solvolysis rates were followed in the usual manner according to a conductmetric method described earlier.[8] Conductivity readings were taken by using a conductivity meter (Model CM-50AT and CM-60S equipped with time interval unit and prints, Toa Electronic Ltd.). Solvolysis was followed by taking at least 20 points at appropriate intervals for 2.5 half lives. The measurements were made on a 10^{-3}—10^{-4} mol dm^{-3} solution of the starting *p*-nitrobenzoates and in the presence of excess lutidine in a thermostated bath controlled to within ±0.04 °C. The rate constants were obtained graphically. At least two determinations were used for each *p*-nitrobenzoate at each temperature. Rate constants from repeated runs were reproducible with an accuracy of 3%.

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