# Substituent Effects in the Solvolysis of *p*-(2-Substituted Cyclopropyl)-α-Methylbenzyl Chlorides[1)]

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The solvolysis rates of *p*-(*cis*- or *trans*-2-substituted cyclopropyl)-α-methylbenzyl chlorides including electron-donating and electron-attracting substituents relative to a hydrogen substituent were measured in 80% aqueous acetone. The trans isomers were more reactive than the corresponding cis derivatives where cyclopropyl and phenyl groups could not get a most favorable "bisected" conformation for the cyclopropyl group to release electrons to the benzene ring. The relative rates of the trans isomers at 45 °C were best correlated by means of $\sigma_m$ values with a $\rho$ value of −3.14 and a correlation coefficient of 0.97, indicating that the cyclopropane ring was a poor transmitter of a resonance effect. The substituent effects were analyzed by means of the LSFE equation.

The C–C bonds of the cyclopropane ring have, to a greater or lesser degree, the characteristics of C–C double bonds, including more *p*-orbital character than expected for saturated C–C bonds.[2)] The cyclopropyl group can enter into conjugated systems[3,4)] and can become a strong electron donor when it is directly attached to the electron-deficient center.[5)] The superior electron-donating ability of the cyclopropyl group is evidenced quantitatively by the more negative $\sigma^+$ value (−0.41—−0.54)[6–8)] than that of isopropyl (−0.28) and other alkyl groups (−0.25 to −0.32).[9)]

In a previous paper,[6)] we reported the kinetics of the solvolysis of *p*-substituted α-methylbenzyl chlorides in 80% aqueous acetone; the *p*-cyclopropyl derivative reacted 353 times faster than the parent chloride, indicating the strong contribution of a resonance effect in the transition state. However, the relative rate of the *p*-(2,2-dichlorocyclopropyl) derivative to the unsubstituted α-methylbenzyl chloride was only 1.24. The $\sigma^+$ value for the 2,2-dichlorocyclopropyl group estimated from the solvolysis of *p*-(2,2-dichlorocyclopropyl)-α-methylbenzyl chloride and the dissociation of *p*-(2,2-dichlorocyclopropyl)phenylacetic acid in 50% ethanol by means of the LArSR equation[10)] presented by Yukawa and Tsuno, was only −0.02.[6)] Moreover, the parameter $\Delta\bar{\sigma}_R^+$ values which measure the capacities of the substituents to supply electrons by a resonance effect in the LArSR equation were −0.35 and −0.07 for the cyclopropyl and the 2,2-dichlorocyclopropyl groups, respectively. Thus, the replacement of the two hydrogens at the 2-position of cyclopropyl with two chloro substituents caused a remarkable reduction of the resonance exaltation of the cyclopropyl group. Two factors may be responsible for this reduction of the resonance effect. One is the decreasing of the polarizability of $C_1$–$C_2$ bonds due to the strongly electronegative chloro substituent. The other is the conformational change from the most favorable "bisected" conformation in order to release electrons from cyclopropyl to phenyl, due to the repulsion between the cis chlorine atom and the hydrogen atom at the ortho position of the benzene ring.[11,12)]

In order to evaluate the relative contribution of these two factors and to clarify the electronic characteristics of 2-substituted cyclopropyl groups, we have studied the solvolysis of *p*-(*cis*- and *trans*-2-substituted cyclopropyl)-α-methylbenzyl chlorides. The mechanism of this solvolysis reaction was well studied by Tsuno and co-workers.[10b)]

## Results and Discussion

The solvolysis rates of *p*-(2-substituted cyclopropyl)-α-methylbenzyl chlorides in 80% aqueous acetone were determined by conductometric measurements at the initial concentrations of $10^{-5}$ mol dm$^{-3}$. The reproducibilities of the rate constants were within an accuracy of 2%. The rate constants for the bromo and the chloro

Table 1. Solvolysis Rates of *p*-(2-Substituted Cyclopropyl)-α-Methylbenzyl Chlorides in 80%(v/v) Aqueous Acetone

| Substituent | | $k_1\times10^5$ ($s^{-1}$) | | |
|---|---|---|---|---|
| | | 25 °C | 35 °C | 45 °C |
| H | | | | 258[a)] |
| F | *cis* | 2.73 | 8.35 | 24.0 |
| | *trans* | 2.85 | 9.45 | 25.1 |
| Cl | *cis* | 0.896 | 2.96 | 8.71 |
| | *trans* | 1.80 | 5.64 | 16.8 |
| $Cl_2$ | | | | 0.905[a)] |
| Br | *cis* | 0.89 | 2.80 | 8.75 |
| | *trans* | 1.73 | 5.30 | 15.8 |
| $CH_3$ | *cis* | 12.5 | 36.7 | 105 |
| | *trans* | 51.5 | 141 | 387 |
| 1-$CH_3$ | | 12.9 | 36.9 | 99.9 |
| $C_6H_5$ | *cis* | 9.51 | 28.3 | 83.0 |
| | *trans* | 14.7 | 44.0 | 124 |
| $CH_3O$ | *trans* | 19.7 | 59.9 | 163 |
| $COOC_2H_5$ | *cis* | 0.890 | 2.93 | 9.06 |
| | *trans* | 1.53 | 4.80 | 14.8 |
| [$C_6H_5CHClCH_3$] | | | | 0.729[a)], 0.726[b)] |

a) Ref. 6. b) E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).

derivatives thus obtained were identical to those obtained by the acid-base titration method.[6] The obtained rate constants are summarized in Table 1 together with those of the 1-methylcyclopropyl and 2,2-dichlorocyclopropyl derivatives and the parent α-methylbenzyl chloride. The relative rates of solvolysis of *p*-(2-substituted cyclopropyl)-α-methylbenzyl chloride and the activation parameters at 45 °C are listed in Table 2. The $^1$H NMR observation revealed that the product of this solvolysis was the corresponding alcohol.

For all compounds measured, the trans isomers reacted faster than the corresponding geometrical isomers, the cis derivatives (Table 2). $k_{trans}/k_{cis}$ values were in the range of 1.05—3.69 and increased as the van der waals radii of the substituents increased, indicating that these rate differences were caused by the repulsion between the substituent and the hydrogen atom at the ortho position in the phenyl group in the cis derivative. Our results obtained here are consistent with the solvolysis of the geometrical isomers of 2-[*p*-(2-chlorocyclopropyl)phenyl]-2-chloropropane and 2-[*p*-(2-bromocyclopropyl)phenyl]-2-chloropropane in 90% aqueous acetone reported by Kulinkovich and co-workers.[8] Thus, the cis isomers had an energetically less-favorable conformation and could not get a maximum overlap between cyclopropyl $C_1$–$C_2$ bonds and the p-orbital of the benzene ring, leading to the rate depression relative to the trans isomer. The rate deceleration effect of the 1-methyl group for the cyclopropyl group supported this explanation. The $k_{trans}/k_{cis}$ values for a chlorine was 1.93, while $k_{trans}/k_H$=0.065 and $k_{cis}/k_H$=0.034. The rate depression by two chlorine atoms observed for the 2,2-dichlorocyclopropyl group[6] was ascribed mainly to the decreased polarizability of $C_1$–$C_2$ bonds of the cyclopropyl group, due to the electronegative behavior of the chlorine atom. These effects of the chlorine substituent obtained here were similar to those observed in the solvolysis of 2-[*p*-(2-chlorocyclopropyl)phenyl]-2-chloropropanes.[8]

It was very interesting that the methoxyl group (trans),[13] a strong electron-donating substituent by a resonance effect, retarded the reaction rate by a factor of 0.63. The phenyl group (trans) also decreased the reaction rate by a factor of 0.48. The $\log k/k_0$—$\log k/k_0$ plot of the relative rates of solvolysis between the *m*-, *p*-substituted α-methylbenzyl chlorides and the *p*-(*trans*-2-substituted cyclopropyl)-α-methylbenzyl chlorides under the same conditions showed a linear relation for the *m*-derivatives but not for the *p*-derivatives as illustrated in Fig 1. Indeed, $\log k_X/k_H$ values for *p*-(*trans*-2-substituted cyclopropyl)-α-methylbenzyl chlorides were best correlated linearly by $\sigma_m$ ($\rho$ value: −3.14, *r*:[14] 0.972) rather than $\sigma_p$ and $\sigma^+$. This correlation confirmed that the cyclopropane ring was a poor transmitter of a resonance effect. There have been some experimental observations that the transmission of the conjugation through the cyclopropane ring is smaller than that through carbon-carbon double bonds.[5,15]

In a previous study, we succeeded in the estimation of the relative importance of an inductive effect and a resonance effect contributing to the dissociation of the 2-substituted 1-cyclopropanecarboxylic acids by means of Yukawa and Tsuno's treatment.[15b] A linear substituent free energy (LSFE) equation presented by Yukawa and Tsuno is considered the most useful for the estimation of the relative contribution of an inductive effect as well as a resonance effect in an extended pi-system beyond the original phenyl system.[16–18]

$$\log(k_X/k_H) = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+$$

Here, $\sigma_i$ is the inductive substituent constant and $\sigma_\pi^+$ is a substituent constant which measures the capability of substituents to donate electrons through electronic delo-

Table 2. The Relative Rates and the Activation Parameters of the Solvolysis of *p*-(2-Substituted Cyclopropyl)-α-Methylbenzyl Chlorides in 80%(v/v) Aqueous Acetone at 45 °C

| Substituent | | Relative rate | $k_{trans}/k_{cis}$ (45 °C) | $\Delta H^{\neq}$ kcal mol$^{-1}$ | $-\Delta S^{\neq}$ e.u. |
|---|---|---|---|---|---|
| H[a] | | 1 | | 18.7 | 11.7 |
| F | *cis* | 0.093 | 1.05 | 19.9 | 10.9 |
| | *trans* | 0.097 | | 19.9 | 12.5 |
| Cl | *cis* | 0.034 | 1.93 | 20.78 | 11.9 |
| | *trans* | 0.065 | | 20.3 | 12.4 |
| $Cl_2$[a] | | 0.0035 | | 23.7 | 47.2 |
| Br | *cis* | 0.034 | 1.81 | 20.7 | 12.1 |
| | *trans* | 0.061 | | 20.4 | 11.9 |
| $CH_3$ | *cis* | 0.41 | 3.69 | 19.4 | 11.3 |
| | *trans* | 1.5 | | 18.5 | 11.6 |
| 1-$CH_3$ | | 0.39 | | 18.6 | 13.8 |
| $C_6H_5$ | *cis* | 0.32 | 1.49 | 19.8 | 10.6 |
| | *trans* | 0.48 | | 19.4 | 10.9 |
| $CH_3O$ | *trans* | 0.63 | | 19.6 | 9.70 |
| $COOC_2H_5$ | *cis* | 0.035 | 1.63 | 21.2 | 10.5 |
| | *trans* | 0.057 | | 20.7 | 11.0 |

a) Ref. 6.

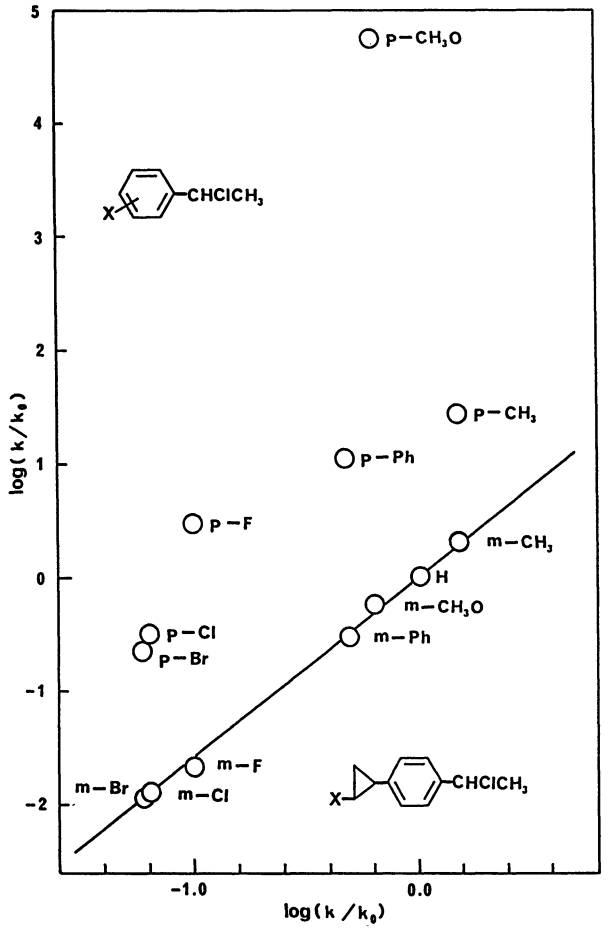



Fig. 1. Log–Log plot of relative rates of solvolysis of *m*- and *p*-substituted α-methylbenzyl chlorides against solvolysis of *p*-(*trans*-2-substituted cyclopropyl)-α-methylbenzyl chlorides in 80% aqueous acetone at 45 °C.

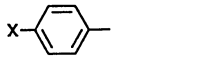
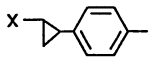
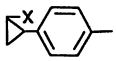
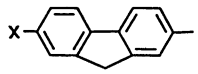
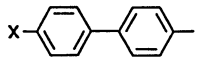
calization. The results of the application of the LSFE equation to the present reactivities are expressed as follows;

$$\log(k_X/k_H) = -3.52\,\sigma_i - 1.89\,\sigma_\pi^+ - 0.08 \text{ (}trans\text{)},\ r = 0.996,^{14)}$$

$$\log(k_X/k_H) = -3.12\,\sigma_i - 1.30\,\sigma_\pi^+ - 0.33 \text{ (}cis\text{)},\ r = 0.913.^{14)}$$

The ratios of the coefficients of $\sigma_i$ and $\sigma_\pi^+$ ($f_i$ and $f_r$, respectively) for the solvolysis of *p*-substituted α-methylbenzyl chlorides, *p*-(2-substituted cyclopropyl)-α-methylbenzyl chlorides, 1-(4′-substituted 4-biphenylyl)-ethyl chlorides,[17] and 1-(7-substituted 2-fluorenyl)ethyl chlorides[18] under the same conditions are summarized in Table 3. It appeared that the relative effectiveness of a transmitting resonance effect could be evaluated from $f_r$ values. The intervention of the cyclopropane ring led to the deceleration of the resonance effect by a factor of 0.1. The transmitting resonance effect of the *trans*-1,2-cyclopropanediyl group was about a third that of *p*-phenylene. These results were predicted from the CNDO calculation for (2-substituted cyclopropyl) methyl cations where the LUMO of the cyclopropyl cation had small coefficients at $C_2$ and $C_3$ so the π-interaction by substituents at these positions was small.[15c] The transmitting inductive effect through the 1,2-cyclopropanediyl group was, however, larger than that through the *p*-phenylene group.

Table 3. Relative $\rho_i$ and $\rho_\pi^+$ Values in the Solvolysis of $ArCHClCH_3$ in 80% Aqueous Acetone

| Ar in $ArCHClCH_3$ | Relative $\rho_i$ ($f_i$) | Relative $\rho_\pi^+$ ($f_r$) |
|---|---|---|
|  a) | 2.17 | 2.78 |
|  b) | 1.54 | 0.28 |
|  b) | 1.37 | 0.19 |
|  c) | 1.00 | 1.00 |
|  d) | 0.70 | 0.69 |

a) Ref. 10b. b) Present study. c) Ref. 18. d) Ref. 17.

## Experimental

All melting points were measured on a YANACO mp hot-stage melting-point apparatus and were uncorrected. The boiling points were also uncorrected. GLC analyses of liquid materials were performed on a YANACO GL80 gas chromatograph. High-performance liquid chromatography was carried out with a JASCO TRIROTOR-V by means of a Finepak SIL column with a Shodex RI SE-51 detector. Preparative-scale LC separations were carried out on a Shodex LC PR100 packed with a MERCK Lichroprep Si60 gel. A mixture of hexane and ethyl acetate was used as an eluent. The geometrical isomers were conveniently separated by this method. The mass spectra were determined at 70 eV using a JEOL D300 instrument. The IR spectra were measured using a JASCO A100 spectrometer. The NMR spectra were determined as a solution in $CDCl_3$ unless otherwise stated, with TMS as an internal standard on a JEOL EX90 spectrometer (90 MHz for $^1H$ and 22.4 MHz for $^{13}C$) and a JEOL FX60 spectrometer (60 MHz for $^1H$ and 15 MHz for $^{13}C$). The assignment of the structure for the geometrical isomers of substituted cyclopropanes was made from the $^{13}C$ NMR spectra, where the cis isomer always resonated at higher fields than did the corresponding trans isomer.[4,19]

All the *p*-(2-substituted cyclopropyl)-α-methylbenzyl chlorides were prepared from the corresponding substituted benzyl alcohols by chlorination with hydrogen chloride in dichloromethane at 3 °C. The obtained chlorides were used for the kinetic measurements without further purification after the removal of dichloromethane under reduced pressure. All the *p*-(2-substituted cyclopropyl)-α-methylbenzyl alcohols were prepared from the corresponding ketones by reduction with $NaBH_4$ in 2-propanol at room temperature or with $LiAlH_4$ in ether at 3 °C.

**(2-Bromo-2-fluorocyclopropyl)benzene:** Sodium *t*-butoxide (100 g) was added over 2 h to a solution of dibromofluoro-

methane (50 g, 0.26 mol) and styrene (52 g, 0.5 mol) in 150 ml of hexane cooled to 3 °C. After the addition had been completed, the mixture was stirred at room temperature for 1 h. The reaction was quenched with 500 ml of water. The reaction mixture was extracted with hexane, washed, dried ($MgSO_4$) and filtered. After the removal of hexane under reduced pressure, the remaining styrene was distilled through a Widmer column fitted with a glass spiral core and the product was distilled carefully through a short column (10 cm): yield 18.5 g (33%); bp 88 °C (7 mmHg, 1 mmHg=133.322 Pa),[20] lit,[21] 71—72 °C (5 mmHg);[20] $^1$H NMR ($CCl_4$) δ=1.52—2.3 (m, 2H, $CH_2$), 2.35—3.1 (m, 1H, CH), and 6.9—7.4 (s, 5H).

**(2-Fluorocyclopropyl)benzene:** This was obtained by the reduction of (2-bromo-2-fluorocyclopropyl)benzene with $LiAlH_4$ in THF.[22] Yield 77%; bp 96—104 °C (40 mmHg).[20] Fractional distillation through a Hempel column gave a geometrical isomer of 80% purity by GC measurements. *Cis:* bp 55—58 °C (10 mmHg),[20] *trans*: bp 96—104 °C (26 mmHg).[20]

***p*-(2-Fluorocyclopropyl)acetophenone:** Iron(III) chloride (1.62 g, 0.01 mol) was added at 10 °C over 10 minutes to a mixture of (2-fluorocyclopropyl)benzene [(1.36 g, 0.01 mol), isomer ratio (4 : 1)], acetyl chloride (0.79 g, 0.01 mol), and carbon disulfide (15 ml). After the addition had been completed, the mixture was stirred at room temperature for an additional hour. The produced complex was hydrolyzed by adding diluted hydrochloric acid. The usual work-up gave *p*-(2-fluorocyclopropyl)acetophenone. Yield 0.86 g (48%). Bp 120—140 °C (6 mmHg).[20] *Cis* isomer: mp 42 °C; $^1$H NMR δ=0.9—2.8 (m, 3H, cyclopropyl), 2.6 (s, 3H, $CH_3$), 4.15—4.5 and 5.15—5.60 (m, 1H, CHF), 7.38 (d, *J*=10 Hz, 2H, PhH), and 7.98 (d, *J*=10 Hz, 2H, PhH); $^{13}$C NMR δ=12.53 (d, $^2J$=10.28 Hz), 21.65 (d, $^2J$=11 Hz), 26.54, 72.59 (d, *J*=223.1 Hz), 128.15, 128.40, 142.05, and 197.59. *Trans* isomer: Oil; $^1$H NMR δ=0.9—2.8 (m, 3H, cyclopropyl), 2.60 (s, 3H, $CH_3$), 4.1—4.4 and 5.0—5.4 (m, 1H, CHF), 7.1 (d, *J*=10 Hz, 2H, PhH), and 7.9 (d, *J*=10 Hz, 2H, PhH); $^{13}$C NMR δ=15.65 (d, $^2J$=9.8 Hz), 22.68 (d, $^2J$=11.5 Hz), 26.48 ($CH_3$), 75.34 (d, *J*=228.7 Hz), 126.05 (CH), 128.49 (CH), 135.21, 144.98, and 197.36.

***p*-(*cis*-2-Fluorocyclopropyl)-α-methylbenzyl Alcohol:** Bp 118 °C (3 mmHg).[20] $^1$H NMR δ=0.8—1.3 (m, 2H, $CH_2$), 1.4 (d, *J*=8 Hz, 3H, $CH_3$), 1.6—2.3 (m, 1H, cyclopropyl), 2.43 (s, 1H, OH), 3.9—4.3 and 5.1—5.41 (m, 1H, CHF), 4.5—6.0 (q, *J*=8 Hz, 1H, CH-O), and 7.1 (s, 4H, PhH); $^{13}$C NMR δ=11.62 (d, $^2J$=10.3 Hz, $CH_2$), 21.13 (d, $^2J$=11.1 Hz, CH), 24.97 ($CH_3$), 69.90 (CH-O), 72.34 (d, *J*=247.7 Hz, CF), 125.16 (CH), 128.45 (d, $^3J$=1.3 Hz), 134.97 (d, $^3J$=3.0 Hz), and 143.84.

***p*-(*trans*-2-Fluorocyclopropyl)-α-methylbenzyl Alcohol:** Mp 24 °C. $^1$H NMR δ=0.7—1.3 (m, 2H, $CH_2$), 1.35 (d, *J*=8 Hz, $CH_3$), 1.8—2.6 (m, 1H, PhCH), 2.35 (s, 1H, OH), 3.9—4.1 and 4.9—5.2 (m, 1H, CHF), 4.7 (q, *J*=8 Hz, 1H, CH-O), 6.9 (d, *J*=7 Hz, 2H, PhH), and 7.22 (d, *J*=7 Hz, 2H, PhH); $^{13}$C NMR δ=14.80 (d, $^2J$=11.56 Hz, $CH_2$), 22.24 (d, $^2J$=11.13 Hz, PhCH), 25.09 (CH), 69.84 (CH-O), 75.31 (d, *J*=226.95 Hz), 125.48 (CH), 126.21 (CH), 138.23, and 143.86.

***p*-(*cis*-2-Fluorocyclopropyl)-α-methylbenzyl Chloride:** Mp 43 °C; $^1$H NMR δ=0.8—1.2 (m, 3H, cyclopropyl), 1.78 (d, *J*=8 Hz, 3H, $CH_3$), 4.0—4.4 and 5.0—5.5 (m, 1H, CHF), 5.42 (q, *J*=7 Hz, 1H, CHCl), and 7.3—8.0 (m, 4H, PhH); $^{13}$C NMR δ=11.93 (d, $^2J$=10.27 Hz, $CH_2$), 21.20 (d, $^2J$=10.71 Hz, PhCH), 26.42 ($CH_3$), 58.60 (CHCl), 72.39 (d, *J*=222.0 Hz), 126.27 (CH), 128.65 (d, $^4J$=1.29 Hz), 136.18 (d, $^3J$=3.42 Hz), and 140.77. Found: C, 67.16; H, 6.09%. Calcd for $C_{11}H_{12}FCl$: C, 66.49; H, 6.09%.

***p*-(*trans*-2-Fluorocylopropyl)-α-methylbenzyl Chloride:** Mp 26 °C; $^1$H NMR δ=0.5—1.9 (m, 2H, $CH_2$), 1.9 (d, *J*=7 Hz, 3H, $CH_3$), 2.0—2.8 (m, 1H, PhCH), 3.9—4.2 and 5.0—5.3 (m, 1H, CHF), 4.05 (q, *J*=7 Hz, 1H, CHCl), 7.0 (d, *J*=9 Hz, 2H, PhH), and 7.3 (d, *J*=9 Hz, 2H, PhH); $^{13}$C NMR δ=14.88 (d, $^2J$=9.85 Hz), 22.25 (d, $^2J$=11.56 Hz), 26.37 ($CH_3$), 58.42 (CHCl), 75.15 (d, *J*=226.95 Hz), 126.38 (d, $^4J$=1.0 Hz), 126.56 (CH), 139.31, and 140.79.

***p*-(*cis*-2-Chlorocyclopropyl)-α-methylbenzyl Alcohol:** This was obtained by the reduction of the corresponding acetophenone[12] with $LiAlH_4$ in ether. Bp 119 °C (2 mmHg);[20] $^1$H NMR δ=1.0—1.7 (m, 2H, $CH_2$, cyclopropyl), 1.4 (d, *J*=7 Hz, 3H, $CH_3$), 1.8 (s, 1H, OH), 2.0—2.6 (m, 1H, CH), 3.1—3.5 (m, 1H, CH), 4.6—5.1 (q, *J*=7 Hz, CHOH), and 7.2 (s, 4H, Ph); $^{13}$C NMR δ=14.24 ($CH_2$), 22.52, 25.00, 34.45, 70.10 (CHOH), 125.00 (CH), 129.26 (CH), 135.21, and 144.12.

***p*-(*trans*-2-Chlorocyclopropyl)-α-methylbenzyl Alcohol:** Bp 135 °C (5 mmHg);[20] mp 39 °C; $^1$H NMR δ=1.2—1.9 (m, 2H, $CH_2$), 1.6 (d, *J*=7 Hz, 3H, $CH_3$), 2.0 (s, 1H, OH), 2.1—2.7 (m, 1H, CH), 3.1—3.5 (m, 1H, CH), 4.8—5.3 (q, *J*=7 Hz, 1H, CHOH), 7.2 (d, *J*=8 Hz, 2H, PhH), and 7.5 (d, *J*=8 Hz, 2H, PhH); $^{13}$C NMR δ=18.56 ($CH_2$), 25.11, 26.45, 35.00, 70.01, 125.51 (CH), 126.10 (CH), 138.80, and 144.01.

***p*-(*cis*-2-Chlorocyclopropyl)-α-methylbenzyl Chloride:** Mp 43 °C; $^1$H NMR δ=0.9—1.7 (m, 2H, $CH_2$), 1.93 (d, *J*=7 Hz, $CH_3$), 2.0—2.6 (m, 1H, CH), 3.1—3.6 (m, 1H, CH), 4.8—5.4 (q, *J*=7 Hz, 1H, CHCl), and 7.0—7.5 (m, 4H, PhH); $^{13}$C NMR δ=14.43 ($CH_2$), 22.55, 26.40, 34.40, 58.57, 126.10 (CH), 129.38 (CH), 136.21, and 141.08; Found:C, 61.73; H, 5.22%. Calcd for $C_{11}H_{12}Cl_2$: C, 61.39, H, 5.62%.

***p*-(*trans*-2-Chlorocyclopropyl)-α-methylbenzyl Chloride:** Mp 35 °C; $^1$H NMR δ=1.2—1.6 (m, 2H, $CH_2$), 1.8 (d, *J*=7 Hz, 3H, $CH_3$), 2.0—2.5 (m, 1H, CH), 2.9—3.3 (m, 1H, CH), 4.8—5.3 (q, *J*=7 Hz, 1H, CHCl), 7.0 (d, *J*=9 Hz, 2H, PhH), and 7.3 (d, *J*=9 Hz, 2H, PhH); $^{13}$C NMR δ=18.68 ($CH_2$), 26.37, 35.00, 58.34, 126.16 (CH), 126.56 (CH), 139.65, and 140.93. Found: C, 62.18; H, 5.30%. Calcd for $C_{11}H_{12}Cl_2$: C, 61.39; H, 5.62%.

**(2-Bromocyclopropyl)benzene:** This was obtained by the treatment of (2,2-dibromocyclopropyl)benzene[23] with diethyl phosphonate in the presence of trimethylamine and water at 90 °C.[24] Bp 100—101 °C (10 mmHg).[20]

**(*cis*-2-Bromocyclopropyl)benzene:** $^1$H NMR ($CCl_4$) δ=1.1—1.7 (m, 2H, $CH_2$), 1.9—2.5 (m, 1H), 3.0—3.4 (m, 1H), and 6.9—7.3 (m, 5H); $^{13}$C NMR δ=14.2 ($CH_2$), 22.1 (PhC), 23.9 (CBr), 126.7, 127.8, 129.1, and 137.0 (ipso).

**(*trans*-2-Bromocyclopropyl)benzene:** $^1$H NMR ($CCl_4$) δ=1.2—1.6 (m, 2H, $CH_2$), 2.1—2.5 (m, 1H), 2.7—3.1 (m, 1H), and 6.7—7.3 (m, 5H); $^{13}$C NMR δ=18.8 ($CH_2$), 21.5 (CBr), 26.8 (CPh), 125.8, 126.4, 128.4, and 139.6 (ipso).

***p*-(*cis*-2-Bromocyclopropyl)acetophenone:** This was prepared by the Friedel-Crafts reaction using aluminium(III) chloride as a catalyst and carbon tetrachloride as solvent. Mp 151 °C; $^1$H NMR δ=0.9—1.5 (m, 1H), 1.0—1.8 (m, 2H, $CH_2$), 2.5 (s, 3H, $CH_3$), 3.0—3.5 (m, 1H), 7.1—7.4 (d, 2H, *J*=7 Hz, Ph), and 7.7—8.0 (d, *J*=7 Hz, 2H, PhH); $^{13}$C NMR δ=14.72 ($CH_2$), 22.12 (CH), 23.75 (CH), 26.51 ($CH_3$), 127.87 (CH), 129.18 (CH), 135.58, 142.73, and 197.42 (C=O); MS *m/z* 240, 238, 159, and 43.

***p*-(*trans*-2-Bromocyclopropyl)acetophenone:** This was prepared by the same method described above for the cis isomer. Mp 53 °C; $^1$H NMR δ=1.2—1.7 (m, 2H, $CH_2$), 2.1—2.6 (m, 1H, CH), 2.45 (s, 3H, $CH_3$), 2.8—3.1 (m, 1H, CH), 6.8—7.1 (d,

$J$=8 Hz, PhH), and 7.6—7.8 (d, $J$=8 Hz, 2H, PhH). $^{13}$C NMR $\delta$=19.73 ($CH_2$), 21.52 (CH), 26.45, 26.91, 125.85, 128.52 (CH), 135.44, 145.38, and 197.11 (C=O); MS $m/s$ 240, 238, 159, and 43.

***p*-(*cis*-2-Bromocyclopropyl)-α-methylbenzyl Alcohol:** Mp 53.5 °C; $^1$H NMR $\delta$=1.1—1.7 (m, 2H, $CH_2$), 1.4 (d, $J$=7 Hz, 3H, $CH_3$), 1.9 (s, 1H, OH), 2.0—2.5 (m, 1H, CH), 3.0—3.4 (m, 1H, CH), 4.5—4.9 (q, $J$=7 Hz, 1H, CH), and 6.9—7.3 (m, 4H, PhH); $^{13}$C NMR $\delta$=14.40, 21.87, 23.86, 25.00, 70.16, 125.00 (CH), 129.26 (CH), 136.33, and 144.35.

***p*-(*trans*-2-Bromocyclopropyl)-α-methylbenzyl Alcohol:** Oil; $^1$H NMR $\delta$=1.2—1.6 (m, 2H, $CH_2$), 1.38 (d, $J$=7 Hz, 3H, $CH_3$), 2.1—2.5 (m, 1H, CH), 2.6 (s, 1H, OH), 2.75—3.05 (m, 1H, CH), 4.65 (q, $J$=7 Hz, 1H, CH), 6.8 (d, $J$=12 Hz, 2H, PhH), and 7.1 (d, $J$=12 Hz, 2H, PhH); $^{13}$C NMR $\delta$=18.79, 21.41, 25.06 ($CH_3$), 26.59, 69.93 (CH), 125.79 (CH), 126.02 (CH), 138.88, and 144.12.

***p*-(*cis*-2-Bromocyclopropyl)-α-methylbenzyl Chloride:** Oil; $^1$H NMR $\delta$=1.1—1.8 (m, 2H, $CH_2$), 1.82 (d, $J$=7 Hz, $CH_3$), 2.0—2.5 (m, 1H, CH), 3.1—3.5 (m, 1H, CH), 4.8—5.3 (q, $J$=7 Hz, 1H, CHCl), and 7.3—7.6 (m, 4H, PhH); $^{13}$C NMR $\delta$=14.46 ($CH_2$), 21.75 (CH), 23.86 (CH), 26.34 ($CH_3$), 58.51 (CHCl), 126.02 (CH), and 129.76 (CH); MS $m/z$ 262, 260, 225, 223, 181, and 179.

***p*-(*trans*-2-Bromocyclopropyl)-α-methylbenzyl Chloride:** Oil; $^1$H NMR $\delta$=1.2—1.8 (m, 2H, $CH_2$), 1.8 (d, $J$=7 Hz, 3H, $CH_3$), 2.0—2.6 (m, 1H, CH), 2.7—3.2 (m, 1H, CH), 4.8—5.3 (q, $J$=7 Hz, 1H, CHCl), 7.0 (d, $J$=11 Hz, 2H, PhH), and 7.3 (d, $J$=12 Hz, 2H, PhH); $^{13}$C NMR $\delta$=18.96 ($CH_2$), 21.50, 26.33 ($CH_3$), 26.50, 58.34 (CHCl), 126.07 (CH), 126.59 (CH), 139.86 (CH), and 141.00 (CH); MS $m/z$ 262, 260, 259, 258, 225, 223, 181, and 179.

**(*trans*-2,2-Dichloro-3-methylcyclopropyl)benzene:** This was prepared by dichlorocarbene addition to *trans*-β-methylstyrene. Bp 119 °C (16 mmHg);[20] $^1$H NMR $\delta$=1.4 (d, $J$=6 Hz, 3H, $CH_3$), 1.8—2.1 (m, 1H), 2.4 (d, $J$=11 Hz, 1H), and 7.3 (s, 5H, PhH);[6,23] $^{13}$C NMR $\delta$=14.80 ($CH_3$), 29.76 (CH), 41.69 (PhCH), 66.59 ($CCl_2$), 127.39, 128.21, 128.68, and 134.91 (ipso).

**(*cis*-2,2-Dichloro-3-methylcyclopropyl)benzene:** This was prepared by dichlorocarbene addition to *cis*-β-methylstyrene.[22] Bp 121 °C (16 mmHg);[20] $^1$H NMR $\delta$=1.10 (d, $J$=6 Hz, 3H, $CH_3$), 1.8—2.3 (m, 1H), 2.8 (d, $J$=11 Hz, 1H), and 7.28 (s, 5H, PhH); $^{13}$C NMR $\delta$=11.90 ($CH_3$), 29.43, 36.06, 65.27 ($CCl_2$), 127.15, 128.27 (CH), 130.47 (CH), and 133.00.

**(*trans*-2-Methylcyclopropyl)benzene:** This was prepared by the reduction of (*trans*-2,2-dichloro-3-methylcyclopropyl)benzene with sodium and ethanol in a 47% yield, bp 80 °C (15 mmHg);[20] $^1$H NMR $\delta$=0.6—1.0 (m, 3H), 1.1 (d, $J$=8 Hz, 3H, $CH_3$), 1.3—1.6 (m, 1H), and 6.8—7.3 (m, 5H); $^{13}$C NMR $\delta$=17.60 ($CH_2$), 17.94 (CH), 19.07 ($CH_3$), 24.37 (PhCH), 125.04, 125.40, 128.12, and 143.90 (ipso).

**(*cis*-2-Methylcyclopropyl)benzene:** This was obtained by the reduction of (*cis*-2,2-dichloro-3-methylcyclopropyl)benzene using sodium and ethanol in an 8% yield. The reduction of (*cis*-2-chloro-3-methylcyclopropyl)benzene, itself prepared from $LiAlH_4$ reduction in THF from the dichloro derivative,[23] afforded a better yield (25%). Bp 75—77 °C (12 mmHg);[20] $^{13}$C NMR $\delta$=10.8 ($CH_2$), 12.6 (CH), 13.6 ($CH_3$), 21.1 (C-Ph), 125.5, 127.7 (CH), 129.2 (CH), and 139.4 (ipso).

***p*-(*cis*-2-Methylcyclopropyl)acetophenone:** Anhydrous aluminium(III) chloride (2.1 g, 15 mmol) was added at −35 °C for 1 h to a mixture of (*cis*-2-methylcyclopropyl)benzene (2.1 g, 15 mmol), acetyl chloride (1.2 g, 15 mmol) and chloroform (10 ml). After the usual work-up, *p*-(*cis*-2-methylcyclopropyl)-acetophenone (1.2 g) was obtained in a 40% yield. Bp 106—109 °C (4 mmHg);[20] $^1$H NMR $\delta$=0.5—1.7 (m, 3H), 0.76 (d, $J$=6 Hz, 3H, $CH_3$), 1.8—2.7 (m, 1H), 2.57 (s, 3H, $CH_3$), 7.25 (d, $J$=8 Hz, 2H, PhH), and 7.87 (d, $J$=8 Hz, 2H, PhH); $^{13}$C NMR $\delta$=11.56 ($CH_2$), 13.32 (CH), 13.67 ($CH_3$), 21.41 (CH), 26.48 ($CH_3$), 127.90 (CH), 129.04 (CH), 134.67, 145.78, and 197.59 (CO); MS $m/z$ 174, 159, and 43.

***p*-(*trans*-2-Methylcyclopropyl)acetophenone:** This was obtained by the same method used for the *cis* isomer in a 43% yield. Bp 115 °C (6 mmHg);[20] $^1$H NMR $\delta$=0.75—1.85 (m, 4H), 1.35 (m, 3H, $CH_3$), 2.58 (s, 3H, $CH_3$), 7.15 (d, $J$=14 Hz, 2H, PhH), and 7.95 (d, $J$=14 Hz, 2H, PhH); $^{13}$C NMR $\delta$=18.73, 18.96, 19.25 ($CH_3$), 24.60 (CH), 26.37 ($CH_3$), 125.22 (CH), 128.35 (CH), 134.27, 150.21, and 197.26 (C=O); MS $m/z$ 174, 159, and 43; Found: C, 81.03; H, 8.23%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%; Found: $m/z$ 174.1043. Calcd for $C_{12}H_{14}O$: 174.1045.

***p*-(*cis*-2-Methylcyclopropyl)-α-methylbenzyl Alcohol:** Oil; $^1$H NMR $\delta$=0.5—1.3 (m, 3H), 1.5 (d, $J$=7 Hz, 3H, $CH_3$), 1.5—2.0 (m, 1H), 2.0 (s, 1H, OH), 4.8 (q, $J$=7 Hz, 1H), and 7.2 (s, 4H, PhH); $^{13}$C NMR $\delta$=10.93, 12.64, 13.58, 20.76, 24.94, 70.16, 124.85 (CH), 129.20 (CH), 138.72, and 142.87.

***p*-(*trans*-2-Methylcyclopropyl)-α-methylbenzyl Alcohol:** Oil; $^1$H NMR $\delta$=0.6—1.6 (m, 4H), 1.1—1.2 (m, 3H), 1.4 (d, $J$=7 Hz, 3H, $CH_3$), 2.4 (s, 1H, OH), 4.7 (q, $J$=7 Hz, 1H, CHOH), 6.8 (d, $J$=9 Hz, 2H, PhH), and 7.1 (d, $J$=9 Hz, 2H, PhH); $^{13}$C NMR $\delta$=17.48, 17.82, 19.02, 24.14, 25.00, 70.16, 125.28 (CH), 125.62 (CH), 142.70, and 143.27; Found: $m/z$ 176.1198. Calcd for $C_{12}H_{16}O$: M, 176.1201.

***p*-(*cis*-2-Methylcyclopropyl)-α-methylbenzyl Chloride:** Oil; $^1$H NMR $\delta$=0.3—1.3 (m, 3H), 0.6—0.8 (m, 3H, $CH_3$), 1.4—2.1 (m, 1H), 1.8 (d, $J$=7 Hz, 3H, $CH_3$), 5.0 (q, $J$=7 Hz, 1H, CHCl), and 6.8—7.5 (m, 4H, PhH); $^{13}$C NMR $\delta$=11.10, 12.84, 13.61, 20.81, 26.42, 58.82, 125.93, 129.29, 139.74, and 139.88.

***p*-(*trans*-2-Methylcyclopropyl)-α-methylbenzyl Chloride:** Oil; $^1$H NMR $\delta$=0.6—1.6 (m, 4H), 1.2 (s, 3H, $CH_3$), 1.8 (d, $J$=7 Hz, 3H, $CH_3$), 5.0 (q, $J$=7 Hz, 1H, CHCl), 7.0 (d, $J$=9 Hz, 2H, PhH), and 7.3 (d, $J$=9 Hz, 2H, PhH); $^{13}$C NMR $\delta$=17.74 ($CH_2$), 18.19 (CH), 19.02 ($CH_3$), 24.06 (CHPh), 26.37 ($CH_3$), 58.77 (CHCl), 125.51 (CH), 126.30 (CH), 139.51, and 144.27; Found: $m/z$ 194.0859. Calcd for $C_{12}H_{15}Cl$: M, 194.0862.

**(1-Methylcyclopropyl)benzene:** This was prepared by the reduction of (2,2-dichloro-1-methylcyclopropyl)benzene with sodium in 2-propanol.[6] Bp 84—85 °C (36 mmHg);[20] $^1$H NMR ($CCl_4$) $\delta$=0.5—0.9 (m, 4H), 1.4 (s, 3H), and 7.1 (m, 5H); $^{13}$C NMR $\delta$=15.60 19.74, 25.73, 125.38, 126.70, 128.11, and 147.02.

***p*-(1-Methylcyclopropyl)acetophenone:** This was obtained in a 60% yield by the Friedel-Crafts reaction using acetyl chloride, aluminium(III) chloride, and chloroform at 7 °C. Bp 105—112 °C (5 mmHg);[20] $^1$H NMR ($CCl_4$) $\delta$=0.7—0.9 (m, 4H, $CH_2$), 1.4 (s, 3H, $CH_3$), 7.2 (d, $J$=9 Hz, 2H, PhH), and 7.8 (d, $J$=9 Hz, 2H, PhH); $^{13}$C NMR $\delta$=16.81, 19.59, 24.85, 26.46, 126.26, 128.35, 134.44, 152.91, and 197.55.

***p*-(1-Methylcyclopropyl)-α-methylbenzyl Alcohol:** Oil; $^1$H NMR $\delta$=0.7—0.9 (m, 4H, $CH_2$), 0.8 (d, $J$=7 Hz, 3H, $CH_3$), 1.4 (t, $J$=3 Hz, 3H, $CH_3$), 3.0 (bs, 1H, OH), 4.7 (q, $J$=7 Hz, 1H, CHOH), and 7.2 (s, 4H, PhH); $^{13}$C NMR $\delta$=15.64 ($CH_2$), 19.37, 24.93, 25.65, 69.82, 125.32 (CH), 126.59 (CH), 142.99, and 146.03.

***p*-(1-Methylcyclopropyl)-α-methylbenzyl Chloride:** Oil; $^1$H

NMR δ=0.6—0.9 (m, 4H), 1.4 (s, 3H, $CH_3$), 2.8 (d, *J*=8 Hz, 3H, $CH_3$), 5.1 (q, *J*=8 Hz, 1H, CHCl), and 7.2 (s, 4H, PhH); $^{13}$C NMR δ=15.80 ($CH_2$), 19.42, 25.49 ($CH_3$), 26.37 ($CH_3$), 58.68 (CHCl), 126.24 (CH), 126.76 (CH), 139.74, and 147.20.

***p*-(*cis*-2-Phenylcyclopropyl)acetophenone:** This was prepared by the Friedel–Crafts reaction at −35 °C, using chloroform as a solvent. Mp 81 °C; $^1$H NMR δ=1.1—1.8 (m, 2H, $CH_2$), 1.8—2.8 (m, 2H), 2.4 (s, 3H, $CH_3$), and 6.6—7.9 (m, 9H, PhH); $^{13}$C NMR δ=11.84 ($CH_2$), 24.09 (CH), 25.40 (CH), 26.37 ($CH_3$), 125.90 (CH), 127.72 (CH), 128.47 (CH), 129.09 (CH), 134.44, 137.29, 144.69, and 197.65 (C=O); IR(neat) 1690 $cm^{-1}$ (C=O).

***p*-(*trans*-2-Phenylcyclopropyl)acetophenone:** This was prepared by the same method for the corresponding *cis* derivative in a 36% yield. Yellow oil; $^1$H NMR δ=1.1—1.8 (m, 2H, $CH_2$), 1.9—2.4 (m, 2H), 2.55 (s, 3H, $CH_3$), and 6.8—8.0 (m, 9H, PhH); $^{13}$C NMR δ=18.85 ($CH_2$), 26.48 ($CH_3$), 28.13 (CH), 28.98 (CH), 125.56 (CH), 125.67 (CH), 125.96 (CH), 128.36 (CH), 128.52 (CH), 134.73, 141.62, 148.45, and 197.37 (C=O); ; IR (neat) 1690 $cm^{-1}$ (C=O).

***p*-(*cis*-2-Phenylcyclopropyl)-α-methylbenzyl Alcohol:** Oil; $^1$H NMR δ=1.2—1.7 (m, 2H, $CH_2$), 1.35 (d, *J*=7 Hz, 3H, $CH_3$), 1.80 (s, 1H, OH), 2.30—2.60 (m, 2H), 4.70 (q, *J*=7 Hz, 1H, CH), and 6.70—7.20 (m, 9H, PhH); $^{13}$C NMR δ=11.47 ($CH_2$), 24.01 (CH), 24.39 (CH), 24.87 ($CH_3$), 70.06 (CH), 124.76 (CH), 125.60 (CH), 127.66 (CH), 129.00 (2CH), 137.68, 138.30, and 143.02.

***p*-(*trans*-2-Phenylcyclopropyl)-α-methylbenzyl Alcohol:** Yellow oil; $^1$H NMR δ=1.2—1.6 (m, 2H), 1.5 (d, *J*=7 Hz, 3H, $CH_3$), 1.7—2.3 (m, 2H), 1.9 (s, 1H, OH), 4.8 (q, *J*=7 Hz, 1H, CH), and 6.8—7.6 (m, 9H, PhH); $^{13}$C NMR δ=18.16, 25.00, 27.67, 27.96, 70.10, 125.45 (CH), 125.67 (CH), 125.79 (CH), 128.29 (CH), 141.73, 142.30, and 143.27.

***p*-(*cis*-2-Phenylcyclopropyl)-α-methylbenzyl Chloride:** Yellow oil; $^1$H NMR δ=1.2—1.6 (m, 2H, $CH_2$), 1.7 (d, *J*=7 Hz, 3H, $CH_3$), 2.3—2.5 (m, 2H), 4.9 (q, *J*=7 Hz, 1H, CHCl), and 6.7—7.2 (m, 9H, PhH); $^{13}$C NMR δ=11.73 ($CH_2$), 23.96 (CH), 24.55 (CH), 26.34 ($CH_3$), 58.66 (CHCl), 125.73 (CH), 125.85 (CH), 127.74 (CH), 129.05 (CH), 138.11, 138.80, and 140.02.

***p*-(*trans*-2-Phenylcyclopropyl)-α-methylbenzyl Chloride:** Yellow oil; $^1$H NMR δ=1.2—1.6 (m, 2H, $CH_2$), 1.8 (d, *J*=8 Hz, 3H, $CH_3$), 1.9—2.3 (m, 2H), 4.8—5.3 (q, *J*=8 Hz, 1H), and 6.9—7.5 (m, 9H, PhH); $^{13}$C NMR δ=18.22, 26.42, 27.73, 28.13, 58.60, 125.67, 125.90, 126.53, 128.35, 140.20, 142.19, and 142.70; Found: *m/z* 256.1021. Calcd for $C_{17}H_{17}Cl$: M, 256.1018.

***p*-(2-Methoxycyclopropyl)acetophenone:** Potassium (3 g, 0.75 mol) was dissolved in a mixture of methanol (25 ml) and hexane (20 ml). The upper layer of hexane was removed with a pipet. To this were added 15-crown-5 (1 ml) and (2-bromocyclopropyl)acetophenone (6.2 g, 26 mmol). The mixture was stirred and maintained at 60 °C for 1 h. After standing overnight, the reaction mixture was poured into water (300 ml) and extracted with benzene (100 ml). *p*-(2-methoxycyclopropyl)acetophenone was separated by column chromatography, using Wakogel-300 and a mixture of hexane and ethyl acetate was used as an eluent. Yield: 0.7 g, 12%. The *trans* isomer was separated by HPLC. Mp 45 °C; $^1$H NMR δ=0.7—1.4 (m, 2H, $CH_2$), 1.8—2.2 (1H, CH), 2.54 (s, 3H, $CH_3$), 3.1—3.4 (m, 1H, C–HO), 3.38 (s, 3H, $CH_3O$), 6.9 (d, *J*=9 Hz, 2H, PhH), and 7.75 (d, *J*=9 Hz, 2H, PhH); $^{13}$C NMR δ=16.86, 23.86, 26.37, 58.08, 63.89, 125.73 128.41, 134.84, 147.20, and 197.14.

***p*-(trans-2-Methoxycyclopropyl)-α-methylbenzyl Alcohol:** Oil; $^1$H NMR δ=0.8—1.3 (m, 1H, CH), 0.8—1.6 (m, 2H, $CH_2$), 1.45 (d, *J*=7 Hz, 3H, $CH_3$), 1.8 (s, 1H, OH), 3.1—3.4 (m, 1H, OCH), 3.4 (s, 3H, $CH_3O$), 4.6—5.1 (q, *J*=7 Hz, 1H, CHOH), 7.0 (d, *J*=9 Hz, 2H, PhH), and 7.3 (d, *J*=9 Hz, 2H, PhH); $^{13}$C NMR δ=15.94 ($CH_2$), 23.24, 25.06, 58.14, 63.77, 70.10, 125.39 (CH), 126.02 (CH), 140.47, and 143.21.

***p*-(*trans*-2-Methoxycyclopropyl)-α-methylbenzyl Chloride:** Oil; $^1$H NMR δ=0.7—1.5 (m, 2H, $CH_2$), 1.6—2.3 (m, 1H, CH), 1.80 (d, *J*=7 Hz, 3H, $CH_3$), 3.1—3.6 (m, 1H, CH–O), 3.4 (s, 3H, $CH_3$), 5.0 (q, *J*=7 Hz, 1H, CHCl), 6.98 (d, *J*=9 Hz, 2H, PhH), and 7.32 (d, *J*=9 Hz, 2H, PhH); $^{13}$C NMR δ=16.06 ($CH_2$), 23.26 (CH), 26.34 ($CH_3$), 58.08 ($CH_3O$), 58.60 (CHCl), 63.32 (CH–O), 126.02 (CH), 126.38 (CH), 140.11, and 141.39.

***p*-(*cis*-2-Ethoxycarbonylcyclopropyl)acetophenone:** This was prepared by the Friedel–Crafts reaction using ethyl *cis*-2-phenyl-1-cyclopropanecarboxylate (7 g, 37 mmol),[25] acetyl chloride (3.2 g, 41 mmol), aluminium(III) chloride (5.5 g, 41 mmol), and 1,2-dichloroethane (45 ml). The reaction was carried out at a temperature over the boiling point of 1,2-dichloroethane. Yield 0.07 g (1%). Oil; $^1$H NMR δ=0.95 (t, *J*=7 Hz, 3H, $CH_3$), 1.15—2.70 (m, 4H), 2.50 (s, 3H, $CH_3$), 3.88 (q, *J*=7 Hz, 2H, $CH_2$), 7.30 (d, *J*=9 Hz, 2H, PhH), and 7.84 (d, *J*=9 Hz, 2H, PhH); $^{13}$C NMR δ=11.49 ($CH_2$), 14.11 ($CH_3$), 22.19 (CH), 25.37 (CH) , 26.53 ($CH_3$), 60.38 ($CH_2$), 128.01 (CH), 129.53 (CH), 135.67, 142.39, 170.61 (C=O, ester), and 197.66 (C=O, ketone).

***p*-(*trans*-2-Ethoxycarbonylcyclopropyl)acetophenone:** This was obtained by the Friedel–Crafts reaction of ethyl *trans*-2-phenyl-1-cyclopropanecarboxylate (3.0 g, 15.8 mmol)[25] with acetyl chloride (4.9 g, 62.4 mmol) at 50 °C. Aluminium(III) chloride (3.5 g, 62 mmol) and 1,2-dichloroethane were used as a catalyst and a solvent, respectively. After the usual work-up, the obtained oil was passed through a column packed with silica gel. Oil; yield: 5 g (16%); $^1$H NMR δ=1.28 (t, *J*=7 Hz, 3H, $CH_3$), 1.2—1.4 (m, 1H), 1.5—1.75 (m, 1H), 1.85—2.10 (m, 1H), 2.55 (s, 3H, $CH_3$), 2.45—2.7 (m, 1H), 4.20 (q, *J*=7 Hz, 2H, $CH_2$), 7.13 (d, *J*=9 Hz, 2H, PhH), and 7.85 (d, *J*=9 Hz, 2H, PhH); $^{13}$C NMR δ=13.78, 17.03, 24.28, 25.48, 25.98, 60.38, 125.72 (CH), 128.17 (CH), 135.03, 145.50, 172.26 (COO), and 196.88 (C=O); IR 1690 $cm^{-1}$ (C=O, ketone) and 1730 $cm^{-1}$ (C=O, ester).

***p*-(*cis*-2-Ethoxycarbonylcyclopropyl)-α-methylbenzyl Alcohol:** This was prepared by the reduction of the corresponding ketone with $NaBH_4$ in 2-propanol. Yellow oil; $^1$H NMR δ=0.91 (t, *J*=7 Hz, 3H, $CH_3$), 1.1—2.7 (m, 4H), 1.39 (d, *J*=7 Hz, 3H, $CH_3$), 2.31 (s, 1H, OH), 3.85 (q, *J*=7 Hz, 2H, $CH_2$), 4.78 (q, *J*=7 Hz, 1H), and 7.23 (s, PhH); $^{13}$C NMR δ=11.23 ($CH_2$), 14.03 ($CH_3$), 21.79 (CH), 25.06 ($CH_3$), 25.23 (CH), 60.19 ($CH_2$), 70.06 (CH), 125.00 (CH), 129.40 (CH), 135.73, 144.32, and 171.03 (C=O).

***p*-(*trans*-2-Ethoxycarbonylcyclopropyl)-α-methylbenzyl Alcohol:** This was obtained by the reduction of the corresponding ketone with $NaBH_4$ in 2-propanol. Oil; $^1$H NMR δ=1.25 (t, *J*=7 Hz, 3H, $CH_3$), 1.44 (d, *J*=7 Hz, 3H, $CH_3$), 1.2—1.7 (m, 2H, $CH_2$), 1.7—2.0 (m, 1H, CH), 2.30 (s, 1H, OH), 2.3—2.7 (m, 1H, CH), 4.15 (q, *J*=7 Hz, 2H, $CH_2$), 4.82 (q, *J*=7 Hz, 1H, CH), 7.00 (d, *J*=9 Hz, 2H, PhH), and 7.25 (d, *J*=9 Hz, 2H, PhH); $^{13}$C NMR δ=14.25 ($CH_3$), 16.99 ($CH_2$), 24.15 (CH), 25.13 ($CH_2$), 25.90 (CH), 60.73 ($CH_2$), 67.00 (CH), 125.57 (CH), 126.31 (CH), 139.30, 144.23, and 173.42 (C=O); IR (neat) 3450 $cm^{-1}$ (C=O); MS *m/z* 234 and 219.

***p*-(*cis*-2-Ethoxycarbonylcyclopropyl)-α-methylbenzyl Chlo-**

**ride:** Oil; $^1$H NMR $\delta$=0.89 (t, $J$=7 Hz, 3H, $CH_3$), 1.05—1.45 (m, 1H), 1.52—1.85 (m, 1H), 1.78 (d, $J$=7 Hz, 3H, $CH_3$), 1.88—2.23 (m, 1H), 2.32—2.70 (m, 1H), 3.84 (q, $J$=7 Hz, 2H, $CH_2$), 5.05 (q, $J$=7 Hz, 1H, CH), and 7.20 (s, 4H, PhH); $^{13}$C NMR $\delta$=11.24 ($CH_2$), 13.98 ($CH_3$), 21.91 (CH), 25.10 (CH), 26.39 ($CH_3$), 58.55 (CHCl), 60.20 ($CH_2$), 126.08 (CH), 129.53 (CH), 136.80, 141.13, and 170.81 (C=O).

***p*-(*trans*-2-Ethoxycarbonylcyclopropyl)-α-methylbenzyl Chloride:** Mp 39 °C; $^1$H NMR $\delta$=1.21 (t, $J$=7 Hz, 3H, $CH_3$), 1.02—2.0 (m, 3H), 1.78 (d, $J$=7 Hz, 3H, $CH_3$), 2.35—2.62 (m, 1H, CH), 4.13 (d, $J$=7 Hz, 2H, $CH_2$), 5.02 (q, $J$=7 Hz, 1H, CHCl), 7.01 (d, $J$=9 Hz, 2H, PhH), and 7.28 (d, $J$=9 Hz, 2H, PhH); $^{13}$C NMR $\delta$=14.25 ($CH_3$), 17.00 ($CH_2$), 24.22 (CH), 25.80 (CH), 26.40, 58.40 (CH), 60.70 ($CH_2$), 126.41 (CH), 126.65 (CH), 140.31, 141.10, and 173.14 (C=O); MS $m/z$ 253, 255, and 218.

**Kinetic Measurement.** 80% aqueous acetone was prepared by mixing corresponding volumes of two components at room temperature. The solvolysis rates were followed in the usual manner according to a conductometric method. Conductivity readings were taken by using a conductivity meter (Model CM-50AT equipped with time interval unit and printer, TOA Electric Ltd.). Solvolysis was followed by taking at least 30 points at appropriate intervals for 2.5 half-lives, and an infinity reading was taken after 10 half-lives. Temperatures of the thermostat bath for the reaction rate experiments were within ±0.03 °C. The rate determination by titration was done by the same procedure as previously published.[6]

The rate constants were obtained graphically. Rate constants from repeated runs were reproducible with an accuracy of 2%.

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