(27), 234 (100), 223 (32), 208 (13), 206 (14), 204 (23). Anal. Calcd for $C_{28}H_{32}N_2O_7$: C, 64.45; H, 6.66; N, 5.78. Found: C, 64.13; H, 6.83; N, 5.50.

(Z)-2-[(2,4,5-Trimethoxy-3-methylphenyl)methylene]-7,9,10-trimethoxy-8,11-dimethyl-4-oxo-1,2,3,4,5,6-hexahydro-1,5-imino-3-benzazocine (10). Formaldehyde (37% solution water, 0.92 mL) was added to a stirred solution of **20** (556.3 mg, 1.14 mmol) in formic acid (2.16 mL) at 50 °C. After being stirred for 1 h at 70 °C, the reaction mixture was poured into water (40 mL) and extracted with chloroform (30 mL × 3). The combined extracts were washed with saturated aqueous $NaHCO_3$ (20 mL), and water (20 mL × 2), dried, and concentrated in vacuo to give a solid, recrystallization of which from AcOEt–ether gave **10** (461.5 mg, 80%) as colorless prisms: mp 200.5–202 °C; IR (KBr) 3380, 1695, 1670 cm^{-1}; UV λ_{max} (log ϵ) 224 (4.44), 277 (4.29), 302 (4.11) nm; ^1H NMR δ 2.17 (3 H, s, Ar CH_3), 2.18 (3 H, s, Ar CH_3), 2.60 (3 H, s, NCH_3), 3.16 (2 H, br, H-6α and H-6β), 3.41 (3 H, s, OCH_3), 3.63 (1 H, br d, H-5), 3.68, 3.72, 3.78, 3.83, 3.91 (each 3 H, s, OCH_3), 4.63 (1 H, s, H-1), 5.89 (1 H, s, C=CH), 6.56 (1 H, s), 8.41 (1 H, s, amide NH); ^{13}C NMR δ 9.3 (q), 9.5 (q), 27.6 (t), 41.6 (q), 56.1 (q), 56.8 (d), 59.2 (d), 59.8 (q), 59.9 (q), 60.2 (q), 60.3 (q), 60.3 (q), 104.5 (d), 110.0 (d), 121.3 (s), 122.7 (s), 124.6 (s), 126.3 (s), 126.3 (s), 133.7 (s), 146.3 (s), 147.4 (s), 149.0 (s), 149.4 (s), 150.0 (s), 152.5 (s), 169.7 (s); MS, m/z (rel intensity) 498 (M^+, 23), 249 (20), 248 (100), 218 (15). Anal. Calcd for $C_{27}H_{34}N_2O_7 \cdot {}^1/_5H_2O$: C, 64.58; H, 6.90; N, 5.58. Found: C, 64.55; H, 7.00; N, 5.35.

Acknowledgment. We thank U. Takeuchi, A. Koike, and I. Kumagai in the Analytical Center of our College for measurement of spectral data (NMR and MS) and microanalytical data. Financial support from the Ministry of Education, Science, and Culture of Japan in the form a Grant-in Aid for Scientific Research is gratefully acknowledged.

Facile Transformation of Substituted Allyl Malonates to Monocarboxylic Acids and Esters by the Reaction with Ammonium Formate Catalyzed by Palladium Complexes

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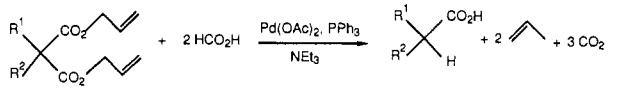
Malonic esters are important intermediates for the synthesis of substituted carboxylic acids or esters. In the malonate method, at first methyl or ethyl malonate is mono- or dialkylated. The hydrolysis of the substituted esters followed by thermal decarboxylation affords substituted carboxylic acids. Although the method is synthetically useful, one drawback is the difficulty in hydrolyzing the substituted malonic esters. Usually the hydrolysis is carried out under rather drastic conditions using a strong base or acid at a high temperature. Therefore, the method cannot be applied to malonates with labile functional groups. To overcome this difficulty, Krapcho and co-workers introduced a good method of the dealkoxycarbonylation to afford mono esters.[1] Substituted malonates undergo the dealkoxycarbonylation to afford monoesters by refluxing in wet DMSO or DMF with an excess of inorganic salts such as NaCN, NaCl, LiI, or LiCl.[2,3] In addition, Ho reported that malonate esters can be converted to carboxylic acids by treatment with iodotrimethylsilane at 100 °C.[4] Also monoesters are obtained by heating substituted malonates with 1 equiv of boric acid at 170–190 °C.[5] In these methods, excess amounts of inorganic salts are required, and the reactions are carried out at somewhat high temperatures.

We now wish to report a simple method for the conversion of substituted malonate esters into monocarboxylic acids or esters under mild conditions. The present method is an extension of our method for the facile hydrogenolysis of allylic esters with tertiary amine salts (typically triethylamine) of formic acid, catalyzed by a palladium phosphine complex, which proceeds with evolution of carbon dioxide and propylene.[6,7]

This reaction proceeds under nearly neutral conditions at lower temperature without attacking labile functional groups. The method can be carried out easily by refluxing a dioxane solution of diallyl esters of mono- or disubstituted malonic acids and slight excesses of triethylamine and formic acid containing catalytic amounts of palladium acetate and triphenylphosphine for several hours. After workup, substituted carboxylic acids are isolated in good yields (Scheme I). Some examples are shown in Table I. When the reaction is carried out at room temperature, only hydrogenolysis takes place to afford substituted malonic acids.

Also, the preparation of monoesters can be carried out. Allyl ethyl malonate was prepared and mono- or dialkylated. The products were subjected to the reaction with HCO_2H–NEt_3 in the presence of the palladium catalyst. In this way ethyl esters were obtained as shown in Scheme II. Some results are given in Table II.

Scheme I



Scheme II

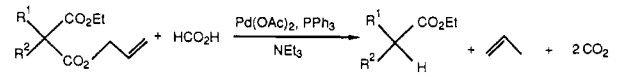
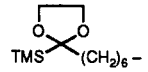


Table I. Preparation of Monocarboxylic Acids[a]

run	R^1	R^2	yield,[b] %
1	n-C_6H_{13}	H	80
2	n-C_6H_{13}	$PhCH_2$	83
3	t-$BuPh_2SiO(CH_2)_4$	H	67
4	$AcO(CH_2)_4$	$PhCH_2$	86

[a] Malonate 0.7 mmol, $Pd(OAc)_2$ 2%, PPh_3 8%, HCO_2H 2.5 equiv, NEt_3 3.3 equiv, dioxane 6 mL, reflux 5 h. [b] Isolated yield.

Table II. Preparation of Monoesters[a]

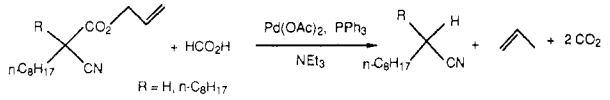
run	R^1	R^2	time, h	yield,[b] %
5	THPO–$(CH_2)_4$	H	7.0	70
6	THPO–$(CH_2)_4$	$PhCH_2$	7.5	90
7		EtO_2CCH_2	5.0	96

[a] Malonate 0.7 mmol, $Pd(OAc)_2$ 2%, PPh_3 8%, HCO_2H 1.25 equiv, NEt_3 1.30 equiv, dioxane 6 mL, reflux. [b] Isolated yield.

(1) For a review, see: Krapcho, A. P. *Synthesis* **1982**, 805, and references therein.
(2) Krapcho, A. P.; Weimaster, J. F.; Eldridge, J. M.; Jahngen, E. G. E.; Lovey, A. J.; Stephens W. P. *J. Org. Chem.* **1978**, *43*, 138.
(3) Krapcho, A. P.; Gadamasetti, G. *J. Org. Chem.* **1987**, *52*, 1880.
(4) Ho, T. L. Synth. *Commun.* **1979**, *9*, 233.
(5) Ho, T. L. *Synth. Commun.* **1979**, *9*, 609.
(6) Tsuji, J.; Yamakawa, T.; Mandai, T. *Tetrahedron Lett.* **1979**, 613.
(7) We have reported the palladium-catalyzed dealkoxycarbonylation of allyl β-keto carboxylates to afford ketones: Tsuji, J.; Nisar, M.; Shimizu, I. *J. Org. Chem.* **1985**, *50*, 3416.

0022-3263/89/1954-5395$01.50/0

Scheme III



The method reported in this paper has several advantages. In particular the reaction can be carried out under nearly neutral conditions without attacking labile functional groups. For example, an acetal (run 7), tetrahydropyranyl ethers (runs 5, 6), and esters (runs 4, 7) remained intact as shown in the tables. The reaction is clean because only carbon dioxide and propylene are byproducts of this reaction.

Similarly, substituted allyl cyanoacetates can be converted to nitriles. Monitoring the reaction by TLC indicated that the cleavage of the allyl group to form the cyanoacetic acid proceeds rapidly, but the decarboxylation is a slow step and takes more than 10 h of heating in dioxane. Allyl octylcyanoacetate and allyl dioctylcyanoacetate were subjected to the palladium-catalyzed reaction with HCO_2H–NEt_3 in refluxing dioxane. The esters disappeared rapidly, but the decarboxylation was a slow step. Decanenitrile (83.7%) and 2-octyldecanenitrile (80.5%) were obtained in good yields (Scheme III).

Experimental Section

General Techniques. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken in $CDCl_3$ as a solvent. Chemical shifts are given in δ units relative to tetramethylsilane as an internal standard. HRMS spectra were taken with JEOL-JMS-DX303 HF. The purity of all compounds, except octanoic acid and decanenitrile, was judged to be higher than 95% by ^1H and ^{13}C NMR spectral determination.

Dealloxycarbonylation of Diallyl Malonates to Monocarboxylic acids. Preparation of 2-Benzyloctanoic Acid. Diallyl benzylhexylmalonate (5.27 g, 14.7 mmol), $Pd(OAc)_2$ (66 mg, 0.29 mmol), and PPh_3 (309 mg, 1.18 mmol) were dissolved in dioxane (25 mL). To this solution, a mixture of HCO_2H (1.39 mL, 36.8 mmol) and NEt_3 (6.76 mL, 48.5 mmol) in dioxane (5 mL) was added, and the mixture was refluxed for 10 h. The solvent was removed under reduced pressure, and dichloromethane (100 mL) and 1 N HCl (120 mL) were added. The organic layer was separated, and the carboxylic acid was extracted with saturated aqueous $NaHCO_3$ (total 120 mL). The aqueous solution was acidified with 3 N HCl and extracted with benzene several times. The benzene solution was dried with $MgSO_4$. 2-Benzyloctanoic acid (3.03 g, 88%) was isolated after evaporation of benzene; HRMS calcd for $C_{15}H_{22}O_2$ m/z 234.1620, found m/z 234.1663.

Dealloxycarbonylation of Allyl Ethyl Malonates to Ethyl Esters. Preparation of Ethyl 2-Benzyl(6-tetrahydropyranyloxy)hexanoate. A mixture of allyl ethyl benzyl (4-(tetrahydropyranyloxy)butyl)malonate (5.30 g, 12.7 mmol), HCO_2H (0.597 mL, 15.9 mmol), NEt_3 (2.3 mL, 16.5 mmol), $Pd(OAc)_2$ (56.9 mg, 0.25 mmol), and PPh_3 (266 mg, 1.01 mmol) in dioxane (25 mL) was refluxed for 8 h. After evaporation of dioxane, 1 N HCl (100 mL) was added, and the mixture was extracted with dichloromethane (70 mL × 2). The organic solution was washed with saturated aqueous $NaHCO_3$ and dried. After evaporation of the solvent, an oily residue was obtained, which was purified by column chromatography on silica gel to give 2-benzyl(6-tetrahydropyranyloxy)hexanoate (3.75 g, 88.4%); HRMS calcd for $C_{15}H_{22}O_3$ (M^+ – 84 (dihydropyran)) m/z 250.1569, found 250.1567.

Dealloxycarbonylation of Substituted Allyl Cyanoacetate. Preparation of 2-Octyldecanenitrile. Allyl dioctylcyanoacetate (209 mg, 0.6 mmol), HCO_2H (34.5 mg, 0.75 mmol), and NEt_3 (78.8 mg, 0.78 mmol) were dissolved in dioxane (4.5 mL), and $Pd(OAc)_2$ (2.7 mg, 0.012 mmol) and PPh_3 (12.6 mg, 0.048 mmol) were added to the solution. The solution was refluxed for 22 h. The solvent was removed under vacuum. 2-Octyldecanenitrile was obtained as an oil (128 mg, 80.5%): HRMS calcd for $C_{18}H_{34}N$ (M^+ – 1) m/z 264.2691, found m/z 264.2707; NMR ($CDCl_3$) δ 0.87 (t, 6 H, J = 6.96 Hz, CH_3), 1.20–1.62 (m, 28 H, CH_2), and 2.44–2.55 (m, 1 H, CHCN). Similarly, decanenitrile was obtained from allyl octylcyanoacetate by refluxing for 10h in dioxane in 83.7% yield; HRMS calcd for $C_{10}H_{18}N$ (M^+ – 1) m/z 152.1439, found m/z 152.1407.

Preparation of Substituted Allyl Ethyl Malonates. Preparation of Allyl Ethyl (4-(Tetrahydropyranyloxy)butyl)malonate. Diethyl malonate (32 g, 0.2 mol) was converted to monoester by the treatment with KOH (16.8 g, 0.3 mol) in aqueous ethanol (60 mL + H_2O, 10 mL) at a room temperature for 3.5 h. Then the monoethyl ester (9.47 g, 71.8 mmol) was treated with allyl alcohol (3 equiv) and dicyclohexylcarbodiimide (17.74 g, 86.1 mmol) in dichloromethane at a room temperature for 4 h. After filtration, the filtrate was concentrated in vacuo. The residue was dissolved in hexane, and the solution was extracted with saturated aqueous $NaHCO_3$. The organic layer was dried and evaporated to give the crude ester, which was purified by distillation (bath temperature 107 °C, 12 mmHg) to give allyl ethyl malonate (8.64 g, 70%). NaH (0.96 g, 40 mmol) was added to DMF (10 mL), to which allyl ethyl malonate (8.6 g, 50 mmol) was added slowly at 0 °C. After 10 min, 4-(tetrahydropyranyloxy)butyl iodide (7.1 g, 25 mmol) in DMF (10 mL) was added slowly, and the mixture was stirred for 30 min at a room temperature. The reaction was quenched by the addition of water (50 mL), and benzene (130 mL) was added. The mixture was washed with 0.5 N HCl and then with saturated aqueous $NaHCO_3$. After evaporation of the solvent, the residue was distilled to give an oil (8.26 g) which was purified further by silica gel column chromatography to afford the pure allyl ethyl ester (6.68 g, 81.5%): ^1H NMR ($CDCl_3$) δ 1.23 (t, 3 H, J = 7.0 Hz, CH_3), 1.35–1.95 (m, 12 H, CH_2), 3.30–3.40 (m, 2 H, COCHCO and OCH_2), 3.43–3.51 (m, 1 H, OCH_2), 3.69–3.75 (m, 1 H, OCH_2), 3.79–3.89 (m, 1 H, OCH_2), 4.17 (q, 2 H, J = 7.0 Hz, OCH_2), 4.52–4.57 (m, 1 H, OCH), 4.60 (d, 2 H, J = 5.8 Hz, OCH_2), 5.21 (dd, 1 H, J = 10.6 and 1.1 Hz, C=CH_2), 5.30 (dd, 1 H, J = 17.0 and 1.5 Hz), and 5.82–5.94 (m, 1 H, CH=C).

Allyl Ethyl Benzyl(4-(tetrahydropyranyloxy)butyl)malonate. NaH (1.46 g, 60.8 mmol) was added to DMF (13 mL) to which allyl ethyl (4-(tetrahydropyranyloxy)butyl)malonate (6.69 g, 20.4 mmol) in DMF (12 mL) was added dropwise. After 5 min, benzyl chloride (7 mL, 60.8 mmol) was added, and the mixture was stirred at a room temperature for 15 min. The reaction was quenched with 0.5 N HCl. After the usual workup, the oily product was purified by silica gel column chromatography to give pure allyl ethyl benzyl(4-(tetrahydropyranyloxy)butyl)malonate (5.33 g, 63%): ^1H NMR ($CDCl_3$) δ 1.23 (t, 3 H, J = 7.0 Hz, CH_3), 1.30–1.90 (m, 12 H, CH_2), 3.25 (s, 2 H, CH_2Ph), 3.35–3.40 (m, 1 H, OCH_2), 3.45–3.54 (m, 1 H, OCH_2), 3.70–3.78 (m, 1 H, OCH_2), 3.82–3.90 (m, 1 H, OCH_2), 4.18 (q, 2 H, J = 7.0 Hz, OCH_2), 4.5–4.65 (m, 3 H, OCH_2, OCH), 5.23 (dd, 1 H, J = 10.6, 1.1 Hz, C=CH_2), 5.31 (dd, 1 H, J = 17.0, 1.5 Hz, C=CH_2), 5.82–5.92 (m, 1 H, CH=C), 7.06–7.10 (m, 2 H, Ar), and 7.18–7.26 (m, 3 H, Ar).

HRMS Data for Other Products: Octanoic acid calcd for $C_8H_{16}O_2$ m/z 144.1150, found m/z 144.1882. 6-Acetoxy-2-benzylhexanoic acid (as the methyl ester) calcd for $C_{16}H_{22}O_4$, m/z 278.1518, found m/z 278.1550. Ethyl 6-(tetrahydropyranyloxy)hexanoate calcd for $C_8H_{16}O_3$ m/z 160.1099 (M^+ – 84 (dihydropyran)), found m/z 160.1081. Diethyl [7-(trimethylsilyl)-7-(1,3-dioxolanyl)heptyl]succinate calcd for $C_{18}H_{33}O_5Si$ (M^+ – 45 (OCH_2CH_3) m/z 357.2097, found m/z 357.2030. 6-(*tert*-Butyldiphenylsiloxy)hexanoic acid (as the methyl ester) calcd for $C_{22}H_{29}O_2Si$ m/z 353.1937, found m/z 353.1982.

Registry No. $CH_3(CH_2)_5CH(CO_2CH_2CH{=}CH_2)_2$, 122846-01-9; $CH_3(CH_2)_5C(CH_2Ph)(CO_2CH_2CH{=}CH_2)_2$, 122846-02-0; t-Bu(Ph)$_2SiO(CH_2)_4CH(CO_2CH_2CH{=}CH_2)_2$, 122846-03-1; AcO$(CH_2)_4C(CH_2Ph)(CO_2CH_2CH{=}CH_2)_2$, 122846-04-2; Pol$(OAC)_2$, 3375-31-3; PPh_3, 603-35-0; $CH_3(CH_2)_6CO_2H$, 124-07-2; $CH_3(CH_2)_5CH(CH_2Ph)CO_2H$, 15327-07-8; t-Bu(Ph)$_2SiO(CH_2)_5CO_2H$, 122846-05-3; ACO$(CH_2)_4CH(CH_2Ph)CO_2H$, 122846-06-4; THPO$(CH_2)_5CO_2Et$, 32437-87-9; THPO$(CH_2)_3CH_2I$, 41049-30-3; allyl ethyl (4-(tetrahydropyranyloxy)butyl)malonate, 122846-07-5; allyl ethyl benzyl(4-(tetrahydropyranyloxy)butyl)malonate, 122846-08-6; ethyl 2-benzyl(6-tetrahydropyranyloxy)hexanoate, 122846-10-0; allyl dioctylcyanoacetate, 122846-12-2; 2-octyldecanenitrile,

57772-74-4; allyl octylcyanoacetate, 122846-13-3; decanenitrile, 1975-78-6; diethyl malonate, 105-53-3; monoethyl malonate, 1071-46-1; allyl ethyl malonate, 15973-34-9; benzyl chloride, 100-44-7; allyl ethyl 2-((ethoxycarbonyl)methyl)-2-[6-(2-(trimethylsilyl)-2-dioxolanyl)hexyl]malonate, 122846-09-7; diethyl [6-(2-(trimethylsilyl)-2-dioxolanyl)hexyl]succinate, 122846-11-1.

Supplementary Material Available: ^{13}C and ^{1}H NMR spectra of the starting allylic esters and the reaction products (34 pages). Ordering information is given on any current masthead page.

Preparation of β-Amino Esters from Ethyl Azidoformate and 1-Alkoxy-1-siloxycyclopropanes

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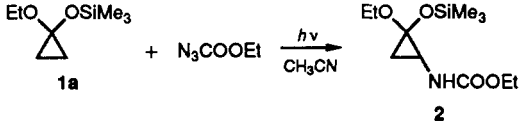
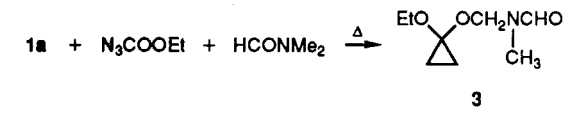
Nitrenes have been known to perform electrophilic reactions such as addition to a carbon–carbon double bond and insertion into a carbon–hydrogen bond. Cyclopropane ring systems possess π-character to some degree and have been well-known to undergo electrophilic attack by proton or Lewis acids to bring about ring-opening. However, the ring-opening of cyclopropane derivatives by nitrene has been relatively unknown except for an intramolecular reaction in a conjugate position to afford an azetine derivative.[1] Limited examples have been reported as to an analogous reaction of a cyclopropane with a carbene.[2] A silyl acetal functionality possesses a highly electron donating character and is easily transformed to an ester group. Indeed, a variety of reactions of the silyl acetal derivatives for preparation of ester derivatives have been reported,[3] including the reaction of ketene silyl acetals with nitrenes to give α-amino esters.[4] Thus, we thought that cyclopropanes with their electron density enhanced by the silyl acetal substituents would react with a nitrene to yield β-amino esters.

Photolysis of a CH_3CN solution containing ethyl azidoformate and 1-ethoxy-1-(trimethylsiloxy)cyclopropane (**1a**) at room temperature for 48 h[4a] gave a product **2**, which was derived from insertion of (ethoxycarbonyl)nitrene into a cyclopropyl C–H bond of **1a** to maintain the cyclopropane ring intact.



1a **2**

Thermolysis of **1a** in DMF did not apparently afford a product due to a reaction of the nitrene with **1a**, but instead gave a product assigned as **3**. The mechanism of formation of **3** is unclear at this time.



3

However, thermolysis of **1a** in DMSO realized opening of the cyclopropane ring by the nitrene. Thus, a solution composed of ethyl azidoformate (2 mmol), **1a** (5 mmol), and DMSO (10 mL) was heated at 120 °C until 2 mmol of N_2 had been evolved (3 h). Then, the reaction mixture was poured into water and extracted with ether. After evaporation of the ether, the residue was subjected to silica gel column chromatography ($CCl_4 \rightarrow CCl_4/Et_2O$) to afford 3-aminopropionate **4a** in 69% yield. ^{1}H and ^{13}C NMR, IR, and mass spectra were in accordance with the assigned structure. As to the mechanism of the formation of **4a**, we thought that two pathways may be possible candidates as shown in Scheme I. One includes insertion of the nitrene into a C–C bond of the cyclopropane ring to form an azetidine intermediate **5** (path A),[5] and the other involves electrophilic attack of the nitrene upon the σ-bond of the ring to induce ring-opening followed by immediate elimination of the electrofugal silyl group (path B).[6] At this stage, we do not have sufficient evidence to prove which of the two pathways operates preferentially. However, path A may be less likely since intermolecular insertion reactions of nitrenes into the C–C bond of the cyclopropane ring have not been reported. Furthermore, Kuwajima et al. have shown that upon reacting 1-alkoxy-1-siloxycyclopropanes with $TiCl_4$, electrophilic attack of the metal on the ring brings about ring cleavage followed by desilylation to generate the titanium homoenolate.[7] DMSO has been known to be an effective trap of nitrenes to result in the formation of sulfoximines,[8] although (ethoxycarbonyl)nitrene has been reported to perform an oxygen transfer from the sulfoxide.[8c] Thus, although we tentatively assumed in Scheme I that the reaction proceeds via attack of the free nitrene upon **1a**, the actual species for the reaction with **1a** might be an intermediate generated from the reaction of the nitrene with DMSO. It might be attributable to intervention of this intermediate that the production of **4a** was attained in DMSO but not in CH_3CN or DMF. The intermediate would not be *N*-(ethoxycarbonyl)dimethylsulfoximine because a nucleophilic character of the sulfoximines[9] seems to be inconsistent with attack on the electron-rich cyclopropane ring of **1a** and, in the reaction with 2-methyl-1-methoxy-1-(trimethylsiloxy)cyclopropane (**1b**), preferential attack upon C-2 with an electron donating substituent over C-3

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(6) A route in which a zwitterion intermediate **6** generated in path B affords **5** by bond-forming between negative and positive charge centers may not be excluded. Its possibility, however, seems to be diminished since loss of the silyl group from a siloxycarbinyl cation is anticipated to be very rapid: Tu, C. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 5287.
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