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Regioselectivity in the Cycloaddition Reactions of *t*-Butyl Trimethylsilyl Thioketone with 1,3-Butadienes

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Thermal cycloaddition of *t*-butyl trimethylsilyl thioketone (**1**) with 2-substituted dienes such as isoprene and 2-trimethylsilyloxy-1,3-butadiene occurred smoothly at 80℃ to afford regioiomeric mixtures of cycloadducts. On the other hand, similar treatment of **1** with 1-substituted dienes such as *trans*-1,3-pentadiene, 1-methoxy- and 1-acetoxy-1,3-butadiene and Danishefsky's diene afforded a single regioisomeric adduct, respectively. Protodesilylation of the silylated adducts **8** and **11** could also be performed with ease.

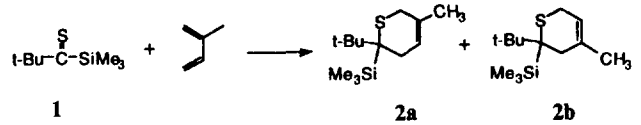
Introduction

Thioacylsilanes have received increasing attention in recent years due to the high reactivity of the carbon-sulfur double bond, which makes possible the synthesis of a variety of compounds, containing the Si-C-S unit.[1] Since these compounds undergo facile desilylation with fluoride ion, thioacylsilanes can be used as synthetic equivalents of unstable thioaldehydes and thiocarbonyl anions.

The reactivity and diastereoselectivity in the cycloaddition of thioacylsilanes with dienes were studied.[1b,c] However, the regioselectivity in the cycloaddition was not explored.[2] Here we describe our results concerning the regioselectivity shown in the reaction of a stable aliphatic thioacylsilane, *t*-butyl trimethylsilyl thioketone (**1**) with unsymmetrical 1,3-butadienes, and further protodesilylation of some silylated cycloadducts.

Results and Discussion

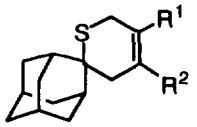
Cycloaddition Reactions of 1 with 2-Substituted Butadienes. When a mixture of *t*-butyl trimethylsilyl thioketone (**1**) and 5-fold excess of isoprene in benzene was heated to 80℃ in a sealed tube, the characteristic blue color of **1** completely disappeared in about 6 h. After purification by preparative tlc (silica gel, *n*-hexane : ether = 8 : 1), a mixture of inseparable regioisomers (**2a** and **2b**) was obtained in 85% yield.



1 **2a** **2b**

The cycloadducts were identified to be 5-methyl-2-*t*-butyl-2-trimethylsilyl-3,6-dihydro-2*H*-thiopyran **2a** and 4-methyl analog **2b** on the basis of spectral data. The mass spectral molecular ion at m/e 242 as well as fragment ions at m/e 185 (M^+-*t*-bu) and 137 (M^+-Me_3Si-S) supported the given structure **2a** and/or its regioisomer **2b**. In the 270 MHz ^{1}H-NMR spectrum, the trimethylsilyl and *t*-butyl protons of **2a** and **2b** appear at δ 0.14, 1.03 and δ 0.16, 1.04, respectively. The methyl protons are not resolved, and appear at δ 1.76 and split into a doublet (J = 1.5 Hz) due to allylic coupling with the vinylic proton. The C-6 methylene protons of **2a** are resolved completely as an AB quartet (J = 15.2 Hz) centered at δ 2.76 and 2.91 while those of **2b** appear as a multiplet at δ 2.95-3.01. The ratio of **2a** and **2b** was determined to be 80 : 20 by ^{1}H-NMR.

In the ^{13}C-NMR spectrum, two pairs of signals due to double-bond carbons of the cycloadducts (**2a** and **2b**) appear at δ 124.30, 133.59 and δ 119.25, 136.59, respectively, and the ratio is approximately 80 : 20. The chemical shifts are very similar to those of the cycloadducts of adamantanethione with isoprene, **3a** [δ 121.2 and 129.9] and **3b** [δ 116.8 and 134.0].[3] These results suggest that the major regioisomer is **2a**.



3a, R^1=CH_3, R^2=H
3b, R^1=H, R^2=CH_3

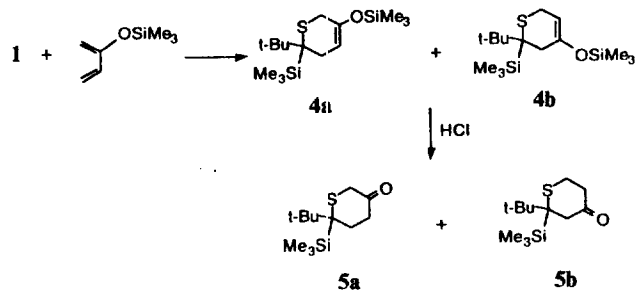
The cycloaddition of **1** with 2-trimethylsilyloxy-1,3-butadiene was performed in benzene at 80℃ for 3 h, and the crude cycloadducts (**4a** and **4b**) were treated with 1 N HCl. After chromatography on silica gel, a mixture of regioisomers

Table 1. ^{1}H-NMR Data of Cycloadducts

Cycloadduct	Me_3Si	*t*-Bu	CH_3	Proton(s) on C-3	C-4	C-5	C-6
2a	0.14, s	1.03, s	1.76, d, J=1.5	2.27-2.30, m	5.53-5.64, m	–	2.76, 2.91, ABq, J=15.2
2b	0.16, s	1.04, s	1.76, d, J=1.5	2.19, brs	–	5.70-5.76, m	2.95-3.01, m
5a	0.23, s	1.06, s	–	*	*	–	3.03, 3.36, ABq, J=16.2
5b	0.18, s	1.09, s	–	*	–	*	
6a major	0.11	1.06	1.28, d, J=6.2	2.08-2.17, m	5.75-5.90, m		3.23-3.27, m
6a minor	0.21	0.97	1.30, d, J=6.2	2.41-2.50, m			
7 major	0.18, s	1.07, s	3.45, s	2.32-2.52, m	5.77-5.89, m	6.15-6.24, m	3.80-4.00, m
7 minor	0.23, s	1.06, s	3.44, s				
8	0.21, s	1.06, s	–	5.27, dd, J=10.6, 1.6	5.69, dd, J=9.3, 6.2	5.80, dd, J=10.6, 6.2	5.90, dd, J=9.3, 2.0
12	0.24, s	1.09, s	–	2.76, 2.09 ABq, J=15.8	–	6.10, d, J=10.8	7.34, d, J=10.8

*The protons appear at δ 2.1-3.0 as a complex multiplet.

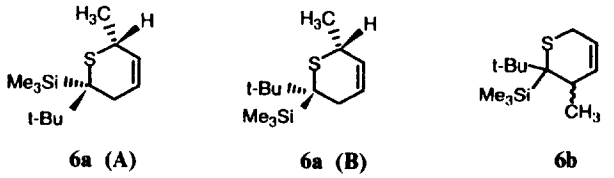
5a and **5b** was obtained in 73% yield.



The regioiomers **5a** and **5b** were isolated and both of them have molecular ion at m/e 244 as well as fragment ions at m/e 187 (M^+-*t*-Bu), 139 (M^+-Me_3Si) and 73 (Me_3Si) in the GC-MS spectrum. In thd 270 MHz ^{1}H-NMR spectrum, the trimethylsilyl and *t*-butyl protons are resolved for each of the regioisomers (see Table 1). The C-6 methylene protons of **5a** appear as an AB quartet (J=16.2 Hz) at δ 3.03 and 3.36, however, other thiacyclohexanone ring protons of **5a** and **5b** appear at δ 2.1-3.0 as a complex multiplet. The relative ratio of **5a** and **5b** was determined as 55 : 45 by ^{1}H-NMR and GC data.

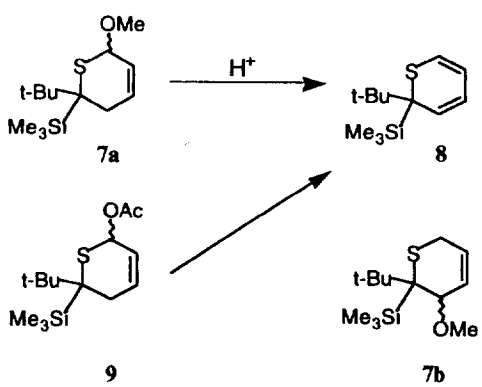
Cycloaddition Reactions of 1 with 1-Substituted Butadienes. Reaction of **1** with *trans*-1,3-pentadiene in benzene at 80℃ afforded a single regioisomer **6a** in 84% yield. No trace of **6b** could be detected. The adduct **6a** is characterized by the C-6 methine proton (δ 3.18-3.32, m), and no absorptions at δ 2.8-3.0. If the adduct were **6b**, the C-6 methylene protons were expected to appear in this region (compare the chemical shifts of the C-6 methylene protons of **2a** and **2b** in Table 1). Such assignment is substantiated by the fact that the chemical shift of the C-3 methylene protons (δ 2.08-2.17 and 2.41-2.50) are similar to those of **2a** and **2b**.

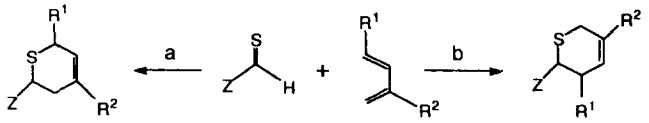
However, the trimethylsilyl (δ 0.11 and 0.21) and *t*-butyl protons (δ 1.06 and 0.97) appear as two singlets, respectively. The methyl protons are also resolved completely at δ 1.27



and 1.29 as a pair of doublets (J=6.2 Hz). These data suggest that the cycloadduct **6a** is a mixture of diastereomers due to the relative stereochemistry of the methyl group attached on C-6. These diastereomers are expected to be formed depending which of the diastereotopic faces of thioacylsilane **1**, *trans*-1,3-pentadiene approaches to. The steric retardation becomes more significant when the bulkier *t*-butyl group of **1** is on the endo position, resulting **6a (B)** to be a minor diastereoisomer. The relative proportion of diastereomer **6a (A)** and **6a (B)** was determined to be 67 : 33 by ^{1}H-NMR.

A similar reaction of **1** with 1-methoxy-1,3-butadiene and chromatographic separation produced **7a** and **8** in 42% and 46% yields, respectively. The product **8** was believed to be formed through the elimination of methanol from the initial cycloadduct **7a** during the silica gel chromatography. This was proved by converting **7a** to **8** in 88% yield in refluxing benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid.





11%	$Z=CH_3CO$, $R^1=CH_3$, $R^2=H$	36%
12%	$Z=CH_3CO$, $R^1=H$, $R^2=OSiMe_2$-t-Bu	43%
70%	$Z=H$, $R^1=CH_3$, $R^2=H$	21%
30%	$Z=SiMe_3$, $R^1=H$, $R^2=OSiMe_2$-t-Bu	3%

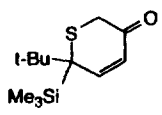
Scheme 1.

The adduct **7a** could be identified by comparing ^{1}H-NMR data with those of **2a**, **2b** and **6a**; there is no signal at δ 2.8-3.0 which are expected for the C-6 methylene protons of the regioisomer **7b**. However, trimethylsilyl (δ 0.18 and 0.23), *t*-butyl (δ 1.07 and 1.06) and methoxy protons (δ 3.45 and 3.44) appear as two singlets, respectively, as observed similarly in the case of **6a**. These results are explained the adduct **7a** to be a mixture of diastereomer. The ratio of diasteromers was determined to be approximately 70 : 30 by ^{1}H-NMR, ^{13}C-NMR, and GC analysis.

When a benzene solution of **1** and 1-acetoxy-1,3-butadiene was heated at 80℃ and then chromatographed on a silica gel plate, only the product **8** could be obtained in 66% yield. The formation of **8** was explained by the elimination of acetic acid from the initial cycloadduct **9** on silica gel. Four vinyl protons of **8** are completely resolved as four sets of double doublets centered at δ 5.27, 5.69, 5.80 and 5.90 in the 300 MHz ^{1}H-NMR spectrum.

The reaction of **1** with Danishefsky's diene (1-methoxy-3-trimethylsilyloxy-1,3-butadiene) in benzene at 80℃ for 2 h afforded a single product **11** (76%) after chromatography. The formation of **11** could be explained by a desilylation, followed by removal of methanol from the initial cycloadduct **10** during chromatography.[4]

10 **11**



12

A 300 MHz ^{1}H-NMR spectrum of **11** showed the C-5 and C-6 vinyl protons as doublets at δ 6.10 and 7.34, respectively, and the C-3 methylene protons as an AB quartet at δ 2.76 and 2.90. A comparision of the chemical shift of the C-3 methylene protons (δ 2.76 and 2.90) of **11** with the C-6 methylene protons of **5a** (δ 3.03 and 3.36) supported structure **11**, but not **12**.

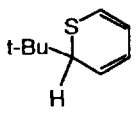
Regiochemistry. E. Vedejs and coworkers reported that the reaction of donor-substituted thioaldehyde with a diene gave cycloadducts with regiochemistry corresponding to advanced C-C bonding in transition state (path a in Scheme 1).[2] On the other hand, acceptor-substituted thioaldehyde reacts in the opposite regiochemical sense with advanced C-S bonding (path b in Scheme 1).[2]

The reversal of regiochemistry have suggested a trend for the reversal in the LUMO polarization of thioaldehydes π^* depending on substituents.[2b] In π-donor-substituted thioaldehydes, carbon has the larger LUMO coefficient and is therefore more electrophilic than sulfur in the cycloaddition with electron rich dienes, while stronger π-acceptor substituents cause a reversal in LUMO polarization.

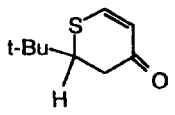
Applying this observation to the reaction of *t*-butyl trimethylsilyl thioketone(**1**) with 2-substituted butadienes, regioselective formation of **5b** and **2b** is expected in the reactions of **1** with 2-trimethylsilyloxy-1,3-butadiene and isoprene, respectively. However, the reaction of **1** with 2-trimethylsilyloxy-1,3-butadiene showed no regioselectivity, and produced 55 : 45 mixture of regioisomers **2a** and **2b**. Moreover the reaction of **1** with isoprene showed the regioselectivity opposite to the E. Vedejs' observation, affording more **2a** than **2b** (**2a** : **2b** = 80 : 20).

Reactions of **1** with 1-subtituted butadienes produced only single regioisomers **6a**, **7a**, and **11** *via* path a in Scheme 1. The trend in the series is clear; however, it is hard to believe that C-C bond formation is advanced in transition state due to the severe steric hindrance. This observed regiochemistry can be rationalized on the basis of the steric approach control. The methyl group of *trans*-1,3-pentadiene severly interferes with the bulky *t*-butyl and trimethylsilyl group of **1** in the transition state on the way to **6b**. Hence, regioisomer **6a** is produced exclusively. The observed pattern of regiochemistry is very similar to the cycloaddition of adamantanethione with butadienes.[3]

Protodesilylation of 8 and 11. The adducts **8** and **11** were protodesilylated in order to obtain the adducts formally obtainable from the cycloaddition of the unstable thioaldehyde, 2,2,-dimethylpropanethial[5], with dienes. The protodesillyation of **8** occurred immediately with *tetra-n*-butylammonium floride (TBAF) in THF-water (one drop) solution at room temperature, affording **13** in 96% yield. The diene **13** is rather unstable and, with time, at room temperature or in solution, the ^{1}H-NMR spectrum becomes complicated. Such instability was observed in the cyclic[1c] and open-chain sulfur dienes,[6]



13



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The reaction with **11** underwent only in boiling THF-water (one drop) with TBAF for 12 h, producing **14** in 89% yield.

In summary, the regioselectivity in the cycloaddition of *t*-butyl trimethylsilyl thioketone (**1**) with 2-substituted-1,3-butadienes was not significant, however, the reaction with 1-substituted-1,3-butadienes proceeded regioselectively; steric hinderance seems to control the regioselectivity. These reactions provide silylated thiacyclohexenes, thiacyclohexanones, thiacyclohexadienes, and thiacyclohexenones in good yields, which are difficult to prepare *via* other routes. The silylated adduct can be protodesilylated with TBAF.

Experimental

^{1}H-NMR spectra were recorded on a Varian EM-360A (60 MHz), a JEOL JSX 270 (270 MHz) or a Bruker 300 MHz spectrometer using tetramethylsilane as an internal standard. ^{13}C-NMR spectra were obtained on a JEOL JSX 270 (58 MHz) spectrometer with $CDCl_3$ as solvent and internal standard. Infrared spectra were recorded on a Mattson Polaris Icon FT IR spectrometer as neat films on potassium bromide plates. Low resolution mass spectra were obstained with a JEOL JMS-DX300 mass spectromer using electron-impact ionization at 70 eV. GC analyses were performed with a Hewlett-Packard 5890A chromatograph using the following conditions; (A) capillary column (HP-1, 0.2 mm ID, 15 m), 100° →10°/min→280° (B) capillary column (Chirasil Val. 0.53 mm ID, 20 m), 100°→10°/min→210°.

2-Trimethylsilyloxy-1,3-butadiene,[7] 1-acetoxy-1,3-butadiene,[8] and Danishefsky's diene[9] were prepared by literature procedures. The remaining dienes were purchased from Aldrich.

Reaction of 1 with isoprene. A benzene (2 m*l*) solution of **1** (70 mg, 0.4 mmol) and isoprene (0.2 m*l*, 136 mg, 2 mmol) was heated in a sealed tube at 80℃ for 6 h until the characteristic blue color of the mixture disappeared completely. Removal of the solvent and excess diene under reduced pressure. The oily residue was chromatographed on a silica gel plate by elution with *n*-hexane-ether (8 : 1). A mixture of regioisomers **2a** and **2b** (80 mg, 85%) was obtained. **2a**: GC (A) 17.5 min; MS m/e 242 (M^+, 6) 227 (M^+-CH_3, 2), 185 (M^+-*t*-Bu, 24), 169 (M^+-Me_3Si, 4), 137 (M^+-Me_3Si-S, 26), 121 (26), 73 (Me_3Si, 100), 57 (*t*-Bu, 49%); ^{13}C-NMR δ 1.29, 23.42, 28.12, 28.45, 29.67, 40.35, 43.35, 124.29, 138.58. **2b**: GC (A) 18.0 min; MS m/s 242 (M^+, 16), 227 (M^+-CH_3, 3), 185 (M^+-*t*-Bu, 20), 137 (M^+-Me_3Si-S, 12), 121 (16), 73 (Me_3Si, 100), 57 (*t*-Bu, 28%); ^{13}C-NMR δ −0.02, 25.12, 25.81, 28.50, 29.69, 40.69, 42.70, 119.24, 136.59.

Reaction of 1 with 2-trimethylsilyloxy-1,3-butadiene. A mixture of **1** (171 mg, 0.98 mmol) and 2-trimethylsilyloxy-1,3-butadiene (435 mg, 3.06 mmol) in benzene (3 m*l*) was heated in a sealed tube at 80℃ for 3 h. After removal of the solvent and excess diene under reduced pressure, the residue was treated with 1 N hydrochloric acid (1 m*l*) in ether (3 m*l*) at room temperature for 12 h. The mixture was treated with aqueous $NaHCO_3$ solution (1 N, 20 m*l*) and extracted with ether (20 m*l*×2). The combined extracts were dried (Na_2SO_4), concentrated, and purified by preparapative tlc (silica gel, dichloromethane) to give 111 mg (68%) of a mixture of regioisomers **5a** and **5b**. IR (KBr, neat) 1720 (C=O) and 1250 (Me_3Si) cm^{-1}. **5a**: GC (A) 24.1 min; MS m/e 244 (M^+, 6) 229 (M^+-CH_3, 8), 187 (M^+-*t*-Bu, 34), 139 (M^+-*t*-Bu, 5), 83 (18), 73 (100%). **5b**: GC (A) 25.0 min; MS m/e 244 (M^+, 5), 229 (M^+-CH_3, 3), 187 (M^+-*t*-Bu, 8), 139 (M^+-Me_3Si-S, 33), 83 (21), 73 (Me_3Si, 100%).

Reaction of 1 with *trans*-1,3-pentadiene (6a). A benzene (2 m*l*) solution of **1** (152 mg, 0.82 mmol) and *trans*-1,3-pentadiene (0.4 m*l*, 270 mg, 4 mmol) was heated at 80℃ for 2 h. After removal of solvent, the residue was chromatographed on silica gel (*n*-hexane : ether=10 : 1) to afford a mixture of diastereomers 2-*t*-butyl-2-trimethylsilyl-3,6-dihydro-6-methyl-2*H*-thiopyran **6a** (176 mg, 84%). **6a** (a mixture of diastereomers): MS m/e 242 (M^+, 5), 185 (M^+-*t*-Bu, 32), 169 (M^+-Me_3Si, 3), 137 (M^+-Me_3Si-S, 18), 121 (10), 73 (Me_3Si, 100), 57 (*t*-Bu, 33%). **6a** (major isomer): ^{13}C-NMR δ 1.22, 20.64, 27.12, 28.30, 33.21, 41.30, 45.41, 130.02, 133.24. **6a** (minor isomer): ^{13}C-NMR δ 1.42, 20.55, 27.65, 28.85, 33.03, 38.89, 46.89, 129.85, 132.95.

Reaction of 1 with 1-methoxy-1,3-butadiene. A mixture of **1** (174 mg, 1 mmol) and 1-methoxy1,3-butadiene (4.9 mmol) in benzene (2 m*l*) was heated at 80℃ for 2 h. After removal of solvent, the residue chromatographed on a silica gel plate (*n*-hexane : ether=8 : 1). The higher fraction gave 108 mg (42%) of **7a** as a mixture of diastereomers. The ratio of the diastereomers was determined as 70 : 30 by ^{1}H, ^{13}C-NMR and GC. The diastereomers could be isolated by the capillary GC under the condition (B), however, both mass spectra are very similar. MS m/e 258 (M^+, 7), 243 (M^+-CH_3, 5), 201 (M^+-*t*-Bu, 3), 175 (25), 153 (M^+-Me_3Si-S, 30), 121 (15), 97 (M^+-Me_3Si-*t*-Bu-OCH_3, 100), 89 (26), 73 (Me_3Si, 82), 57 (*t*-Bu, 21%). **7a** (major isomer): GC (B) 9.8 min (70%); ^{13}C-NMR δ 0.83, 29.23, 32.76, 39.76, 56.09, 72.59, 77.20, 122.62, 124.10. **7a** (minor isomer): GC (B) 9.9 min (30 %); ^{13}C-NMR δ 1.48, 27.42, 33.20, 38.89, 43.65, 75.01, 77.13, 122.61, 124.42.

The lower fraction afforded 103 mg (42%) of **8**: ^{13}C-NMR δ −0.01, 26.24, 42.24, 44.99, 117.79, 121.81, 122.35, 122.49.; MS m/e 226 (M^+, 13), 169 (M^+-*t*-Bu, 23), 153 (M^+-Me_3Si, 100), 137 (M^+-*t*-Bu-S, 7), 138 (10), 73 (Me_3Si, 24%).

To a benzene (2 m*l*) solution of **7a** (108 mg, 0.42 mmol), catalytic amount (10 mg) of *p*-toluenesulfonic acid was added and then refluxed for 1 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography (silica gel, *n*-hexane) to give 83 mg (88%) of **8**.

Reaction of 1 with 1-acetoxy-1,3-butadiene. A benzene (2 m*l*) solution of **1** (200 mg, 1.15 mmol) and 1-acetoxy-1,3-butadiene (440 mg, 3.39 mmol) was heated at 80℃ for 4 h. Work up as described above followed by purification by preparative tlc (silica gel, *n*-hexane) gave 172 mg (66%) of **8**.

Reaction of 1 with Danishefsky's diene. A benzene (3 m*l*) solution of **1** (174 mg, 1.0 mmol) and Danishefsky's diene (557 mg, 3.2 mmol) was heated at 80℃ for 2 h. Work up as described above and purification by preparative tlc (*n*-hexane : ether=1 : 1) gave 183 mg (76%) of **11**. MS m/e 242 (M^+, 10), 241 (24), 227 (M^+-CH_3, 14), 186 (M^+-*t*-Bu, 18), 185 (M^+-*t*-Bu, 55), 153 (M^+-*t*-Bu-S, 7), 137 (M^+-Me_3Si-S, 7), 73 (Me_3Si, 100), 57 (*t*-Bu, 7%); ^{13}C-NMR δ 0.98, 28.14, 40.59, 40.78, 48.91, 122.50, 146.44, 194.36.

Desilylation of 8. To a stirred THF (2 m*l*)-water (one drop) solution of **8** (191 mg, 0.85 mmol), TBAF-THF solution (1 M, 0.9 m*l*, 0.9 mmol) was added at room temperature. The yellow reaction mixture turned red immediately. After 10 min, the solution was treated with water and extracted with ether. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed on a silica gel plate (*n*-hexane : ether=8 : 1) to give 126 mg (96%) of **13**. ^{1}H-NMR (60 MHz, CCl_4) δ 1.16 (s, 9H, *t*-Bu), 2.7-2.9 (m, 1H), 5.2-6.2 (m, 4H); MS m/e 154 (M^+, 7), 153 (53), 138 (M^+-CH_3-1, 7), 97 (M^+-*t*-Bu, 16), 75 (68%).

Desilylation of 11. A solution (1 M) of TBAF in THF (0.35 m*l*, 0.35 mmol) was added to a solution of **11** (80 mg, 0.33 mmol) in THF (2 m*l*) and water (one drop). The mixture was refluxed for 12 h. Purification by preparative tlc (silica

gel, *n*-hexane : ether = 1 : 1) afforded 50 mg (89%) of **14**. ^{1}H-NMR (300 MHz) δ 1.05 (s, 9H, *t*-Bu), 2.58 (dd, 1H, J=14.5 and 16.2 Hz), 2.77 (dd, 1H, J=3.0 and 16.2 Hz), 3.38 (dd, 1H, J=3.0 and 16.2 Hz), 6.18 (d, 1H, J=10.0 Hz), 7.50 (d, 1H, J=10.0 Hz).

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Carbonylation of Bromo(Bromomethyl)Benzenes to Alkyl Carboalkoxyphenylacetates Catalyzed by Cobalt Carbonyl

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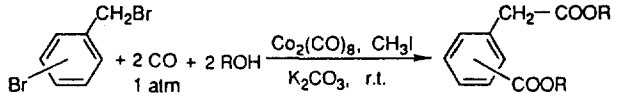
A synthetic method for bis-carbonylation of bromo(bromomethyl)benzenes was described. Alkyl carboalkoxyphenylacetates were easily prepared by the carbonylation of benzylic and arylic bromide moieties in bromo(bromomethyl)benzenes with alcohols in the presence of K_2CO_3, CH_3I, and a catalytic amount of cobalt carbonyl under the atmospheric pressure of carbon monoxide at room temperature in good to excellent yields. The base played a decisive role in the selectivity of product and K_2CO_3 was the best one among bases used.

Introduction

The carbonylation of benzyl- and aryl halides has been systematically developed by the several authors.[1-2] Despite a great amount of the research on the catalytic carbonylation of such organic halides, a little attention has been paid to the catalytic bis-carbonylation of halo(halomethyl)arenes.[3]

Recently, we reported that selective carbonylation of halobenzylhalides gave alkyl (halophenyl)acetates[4] and alkyl (alkoxymethyl)benzoates,[5] respectively depending on reaction conditions used.

We herein wish to report the bis-carbonylation of bromo (bromomethyl)benzenes to give alkyl carboalkoxyphenylacetates catalyzed by cobalt carbonyl.



[1] [2]

Scheme 1

Results and Discussion

Treatments of bromo(bromomethyl)benzenes with alcohol in the presence of a catalytic amount of $Co_2(CO)_8$, K_2CO_3, and CH_3I as a catalyst promoter under the atmospheric pressure of carbon monoxide at room temperature for 24 h gave the corresponding alkyl carboalkoxyphenylacetates in good