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β-Silyl Effects on the Stabilities of Carbanions and Carbon-Centered Radicals Derived from Ethyl Thionacetates, Diethyl Malonates, and Ethyl Acetoacetates

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The effects of an α-Me_3SiCH_2 group on the equilibrium acidities in DMSO of the acidic C−H bonds in esters, including ethyl thionacetate, diethyl malonate, and ethyl acetoacetate, were found to differ from that of an α-$MeCH_2$ group by less than 1 kcal/mol, pointing to little or no stabilizing effect of a β-Me_3Si group on carbanion stabilities. On the other hand, substitution of an α-Me_3SiCH_2 group for one of the acidic hydrogen atoms in these esters to give $Me_3SiCH_2CH_2C(=S)OEt$, $Me_3SiCH_2CH(CO_2Et)_2$, and $Me_3SiCH_2CH(CO_2Et)COCH_3$ was found to decrease the homolytic bond dissociation energies (BDEs) of the remaining acidic C−H bonds by 7.1, 8.2, and 7.1 kcal/mol, respectively, relative to those of the parent esters and by 2.7, 4.5, and 4.4 kcal/mol, respectively, relative to the BDEs of the acidic C−H bonds in the corresponding $MeCH_2$-substituted esters. The differences in BDEs observed between the Me_3SiCH_2- and the $MeCH_2$-substituted ester derivatives are indicative of the presence of 3−5 kcal/mol C−H bond stabilizing effects of β-Me_3Si groups, relative to those of β-Me groups, on the corresponding carbon radicals. The BDE value of the acidic C−H bond in $Me_3CCH_2CH_2C(=S)OEt$ was found to be 86.4 kcal/mol, which represents a 0.6 kcal/mol *increase* in BDE relative to that of the acidic C−H bond in $MeCH_2CH_2C(=S)OEt$. This result demonstrates the absence of a stabilizing effect of a β-*tert*-butyl group on an open-chain carbon-centered radical. This is contrary to an *apparent* 6.4 kcal/mol C−H bond stabilizing effect of the β-*tert*-butyl group in 9-neopentylfluorene, relative to that in fluorene, which is attributed to the relief of steric strain in forming the radical.

Introduction

Both theory and experiment have shown that α-Me_3Si groups are less stabilizing to carbocations than alkyl groups, but generally more stabilizing than hydrogens, whereas a β-Me_3Si groups stabilizes, a carbocation.[1] On the other hand, an α-Me_3Si group stabilizes a carbanion as shown by the increases in the acidities of fluorene and $PhSO_2CH_3$ in DMSO upon the introduction of a Me_3Si group at the acidic site.[2] Information on the effect of β-Me_3Si groups on carbanion stabilities is limited, but existing evidence suggests that the effects are small.[3]

The evidence for stabilizing or destabilizing effects of α- or β-Me_3Si groups on radicals is less clear-cut. The bond dissociation enthalpy for the C−H bond in $Me_3SiCH_2−H$ has been found to be only 0.4 kcal/mol less than that in $Me_3CCH_2−H$,[4] indicating that an α-Me_3Si group has little or no ability to stabilize the corresponding carbon-centered radical relative to that of an α-*t*-Bu group, and recent work in our laboratory has shown that α-Me_3Si groups usually exert small destabilizing effects on carbon-centered radicals.[5]

There is kinetic evidence from rates of hydrogen atom abstraction from Et_4C, Et_4Si, and $(n\text{-}Bu)_3Ge−H$ showing that β-silicon stabilizes a carbon-centered radical, relative to an alkyl group.[6] The effects are small, however, and although the rate for the $Me_3SiCH_2CH_2^{\bullet}$ radical was 7.1 times slower than that for the $Me_3SiCH_2^{\bullet}$ radical toward $(n\text{-}Bu)_3Ge−H$, the rate for the formation of the $Me_3SiCH_2CH_2^{\bullet}$ radical was only 1.2 times slower than that for the $Me_3SiCH_2CH_2CH_2^{\bullet}$ radical and only about 27% slower than that for the $CH_3CH_2CH_2CH_2^{\bullet}$ radical.[6a] Kinetic effects for hydrogen atom abstraction are generally small in such radical reactions because there is relatively little bond breaking in the transition state, and the kinetics are therefore qualitative and difficult to interpret. There is also thermodynamic evidence to support the stabilizing effect of β-Me_3Si groups on carbon-centered radicals, however. Thus, the BDE of the C−H bond in $Me_3SiCMe_2CH_2−H$ has been found to be weaker by 3 ± 1 kcal/mol than that in $MeCMe_2CH_2−H$.[7] (Henceforth, kcal/mol will be abbreviated as kcal.) This result indicates that a β-Me_3Si group stabilizes a carbon-centered radical by about 3 kcal, relative to that of a β-methyl group. Also, pyrolytic cleavages of the C−C bonds in $GCH_2CH_2−CMe_3$ or $GCH_2CH_2−CH_2CH=CH_2$ to give $GCH_2CH_2^{\bullet}$ and $Me_3C^{\bullet}$ or $GCH_2CH_2^{\bullet}$ and $CH_2=CHCH_2^{\bullet}$ radicals, respectively, have been found to be favored by 2.6 ± 1 kcal when G = Me_3Si, compared to when G = H.[8] Furthermore, in the pyrolytic cleavage of a C−C bond in (trimethylsilyl)cyclopropane, the activation enthalpy for the formation of the β diradical, $Me_3SiCH(C^{\bullet}H_2)_2$, is 5.4 kcal lower than that for the formation of the α,β diradical, $Me_3Si^{\bullet}CHCH_2CH_2^{\bullet}$. These experiments also point to a stabilizing effect of about 3 kcal for a β-Me_3Si group on a primary radical, relative to that of a β-methyl group or a β-hydrogen atom.

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On the other hand, the BDE of the acidic C−H bond in 9-((trimethylsilyl)methyl)fluorene, 9-Me_3SiCH_2FlH, has been estimated to be nearly the same as that of the acidic C−H bond in 9-neopentylfluorene, 9-Me_3CCH_2FlH, which has led to the conclusion that the corresponding (tertiary) fluorenyl radicals, 9-$Me_3SiCH_2Fl^•$ and 9-$Me_3CCH_2Fl^•$, are stabilized to nearly the same degree by hyperconjugation involving either a β-Me_3Si or a β-Me_3C group.[10]

In summary, kinetic and thermodynamic studies show that β-Me_3Si groups usually stabilize carbon-centered radicals, whereas α-Me_3Si groups show little or no tendency to do so. The thermodynamic studies indicate that the stabilizing effect of a β-Me_3Si group on a primary carbon-centered radical appears to be about 3 kcal, relative to β-methyl[7] or β-hydrogen,[8] but appears to be negligible toward β-Me_3C in fluorenyl radicals.[10] In the present study, we have used β-Me_3Si-substituted ethyl thionacetates, $Me_3SiCH_2CH_2C(=S)OEt$, diethyl malonates, $Me_3SiCH_2CH(COOEt)_2$, and ethyl acetoacetates, $Me_3SiCH_2CH(COOEt)COCH_3$, to compare effects on BDEs of a β-Me_3Si group with those of β-alkyl groups.

Results and Discussion

For the study of the effect of a β-Me_3Si group on the acidity and BDE of a C−H bond, we first examined β-substituent effects on the acidic C−H bonds in ethyl thionacetates, $GCH_2C(=S)OEt$; a class of esters for which no pK_{HA} or BDE data on substituent effects has previously been obtained.[11] Our method is based on the combination of pK_{HA} values in DMSO with the oxidation potentials of their conjugate bases $E_{ox}(A^-)$ according to eq 1. The BDE differences (ΔBDEs) between the substituted and parent weak acid can be approximated as radical stabilization energies in the absence of appreciable changes in ground state energies.

$$\mathrm{BDE\ (kcal)} = 1.37\mathrm{p}K_{HA} + 23.1E_{ox}(A^-) + 73.3 \quad (1)$$

Ethyl thionacetate, which is readily prepared by the reaction of ethyl acetate with Lawesson's reagent,[12] has a pK_{HA} value 10.8 units (15 kcal) lower and a BDE value about 5 kcal lower than the corresponding values of ethyl acetate. The effects of β-substituents on the acidity and BDEs of the acidic C−H bonds of selected β-substituted ethyl thionacetates were therefore accessible and are summarized in Table 1.

Table 1. pK_{HA} and BDE Values for the Acidic C−H Bonds in α-Substituted Ethyl Thionacetates, $GCH_2C(=S)OEt$, in DMSO

G	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE (kcal)[c]	ΔBDE
H	19.2	−0.405	90.2	(0.0)
CH_3	18.8	−0.590	85.5	4.7
CH_3CH_2	19.1	−0.590	85.8	4.4
t-$BuCH_2$	18.7	−0.548	86.4	3.8
Me_3SiCH_2	18.6	−0.680	83.1	7.1

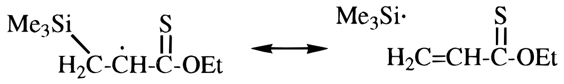
[a] Measured in DMSO (see Table 4). [b] Irreversible oxidation potentials measured by cyclic voltammetry in DMSO using platinum working and auxiliary electrodes and a Ag/AgI reference electrode with 0.1 M $Et_4N^+BF_4^-$ electrolyte and ferrocene/ferrocenium as a standard. [c] Calculated using eq 1.

Table 2. pK_{HA} and BDE Values for the Acidic C−H of 9-Substituted Fluorenes, 9-G-FlH

9-G	pK_{HA}[a]	$E_{ox}(A^-)$[a]	BDE (kcal)[c]	ΔBDE
H (fluorene)	22.6	−1.050	80.0	(0.0)
CH_3CH_2	22.7	−1.221	76.2	3.8
t-$BuCH_2$	20.3	−1.191	73.6	6.4
Me_3SiCH_2	21.3[b]	−1.135[b]	76.3	3.7

[a] All the data are from ref 16, except where specified. [b] pK_{HA}'s were measured in DMSO (see Table 4); irreversible oxidation potentials measured by cyclic voltammetry in DMSO using platinum working and auxiliary electrodes and a Ag/AgI reference electrode with 0.1 M $Et_4N^+BF_4^-$ electrolyte and ferrocene/ferrocenium as a standard. [c] BDEs were calculated using eq 1.

Examination of Table 1 shows that the acidities of the ethyl thionacetates, $GCH_2C(=S)OEt$, vary over a narrow range for substituents where G is Me, Et, Me_3CCH_2, and Me_3SiCH_2 (0.14−0.82 kcal), showing that β-alkyl and β-Me_3Si groups have nearly the same small effects on carbanion stabilities. On the other hand, BDEs of the α-C−H bonds for these substituted thion esters, relative to that of the parent with G = H, were found to be substantially decreased, pointing to appreciable stabilizing effects on the corresponding radicals. For the alkyl groups, the BDEs decrease progressively from 4.7 to 4.4 to 3.8 kcal when G is changed from CH_3, to CH_3CH_2 to Me_3CCH_2, respectively, presumably due to decreasing hyperconjugative effects. The approximately 5 kcal decrease in the BDE observed for α-methyl substitution onto ethyl thionacetate is similar in size to the BDE decreases observed for α-methyl substitution onto acetone,[13] acetophenone,[13] or nitromethane.[14] Analysis of these effects in terms of eq 1 shows that all of these BDE decreases are caused by cathodic shifts in the $E_{ox}(A^-)$ values.[15] A further cathodic shift of 0.132 V (3 kcal) was observed when the *t*-Bu group in *t*-$BuCH_2CH_2C(=S)OEt$ was replaced by a Me_3Si group (Table 1). The BDE when G = Me_3Si is 7.1 kcal lower than that of the parent, G = H, and 3.3 kcal lower than that of an alkyl model, with G = Me_3C. The appreciable radical stabilization energies for a β-Me_3Si group can be attributed to β-silyl hyperconjugation for this radical, as illustrated by **1a** ↔ **1b**.



1a **1b**

This evidence for a sizable stabilizing effect of a β-Me_3Si group on the radical provides support for the earlier kinetic and thermodynamic evidence.[6−8] On the other hand, the β-*tert*-butyl group shows little or no stabilizing effect on the carbon radical, and this is contrary to the result seen from 9-neopentylfluorene.[10]

We have also examined the effect of the β-Me_3Si and β-*tert*-butyl group on fluorene (Table 2). The results summarized in Table 2 agree with those reported by Bausch and Gong except for the ΔBDE between 9-((trimethylsilyl)methyl)fluorene and fluorene. We have observed a ΔBDE of −3.7 (76.3 − 80.0) kcal instead the BDE of −7 (69 − 76) kcal reported. According to our results, the β-Me_3Si group has little or no effect on the

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Table 3. pK_{HA} and BDE Values for the Acidic C−H Bonds in α-Substituted Diethyl Malonates and Ethyl Acetoacetates in DMSO

G	pK_{HA}[a]	$E_{ox}(A^-)$[a]	BDE (kcal)[c]	ΔBDE
		$[GCH(COOEt)_2]$		
H	16.4	−0.022	95.2	(0.0)
CH_3	18.7	−0.352	90.8	4.4
CH_3CH_2	19.1	−0.346	91.5	3.7
Me_3SiCH_2	18.6[b]	−0.480[b]	87.3	8.2
		$[GCH(COOEt)COCH_3]$		
H	14.3[b]	0.005[b]	92.3	(0.0)
CH_3CH_2	16.4[b]	−0.265[b]	89.6	3.7
Me_3SiCH_2	15.8[b]	−0.420[b]	85.2	7.1

[a] Reference 17. [b] pK_{HA}'s were measured in DMSO (see Table 4); irreversible oxidation potentials measured by cyclic voltammetry in DMSO using platinum working and auxiliary electrodes and a Ag/AgI reference electrode with 0.1 M $Et_4N^+BF_4^-$ electrolyte and ferrocene/ferrocenium as a standard. [c] BDEs were calculated using eq 1.

stability of fluorenyl radical, but the β-*tert*-butyl group appears to have a stabilizing effect relative to a β-Me group. We believe, however, that the apparent β-*tert*-butyl stabilization is deceptive and is due to a steric effect rather than an electronic effect, namely a relief of steric strain upon the formation of the 9-neopentylfluorenyl radical. This effect becomes smaller in ((trimethylsilyl)-methyl)fluorene because the Si−C bonds are longer than C−C bonds. These results were augmented by studies of the effects of β-Me_3Si substituents in diethyl malonates and ethyl acetoacetate (Table 3).

The alkyl effects in the α-position on acidities in the diethyl malonates and ethyl acetoacetates are subject to chelation and conformational effects, whereas the alkyl effects on the BDEs are not.[17] The effects of alkyl and β-Me_3SiCH_2 substituents on BDEs in Tables 1 and 3 are remarkably similar. In Table 1 the effects of introducing Me, Et, and Me_3SiCH_2 groups for an acidic hydrogen atom in ethyl thionacetates lead to decreases in BDEs of the acidic C−H bond of 4.7, 4.4, and 7.1 kcal, respectively. In Table 3 the effects of introducing Me, Et, and Me_3SiCH_2 groups for an acidic hydrogen atom in diethyl malonates lead to decreases in BDEs of the acidic C−H bond of 4.4, 3.7, and 8.2 kcal, respectively, and the effects of introducing Et and Me_3SiCH_2 groups for an acidic hydrogen atom in ethyl acetoacetates lead to decreases in BDEs of the acidic C−H bond of 3.7 and 7.1 kcal, respectively. In Table 1 the effects of introducing Et or *t*-$BuCH_2$ groups for an acidic hydrogen atom on the BDEs of the acidic C−H bond differ slightly (4.4 and 3.8 kcal, respectively).

Summary and Conclusions. Substitution of the Me_3SiCH_2 group at the acidic site of ethyl thionacetate, diethyl malonate, and ethyl acetoacetate causes decreases in BDEs of 7−8 kcal relative to the BDE of the parent esters and decreases of about 4 kcal relative to the BDEs of the ethyl-substituted esters. These BDE decreases are rationalized in terms of hyperconjugation effects that are larger for the Me_3SiCH_2 group by 3−4 kcal than for alkyl groups, including a Me_3CCH_2 group in an ethyl thionacetate. In contrast, the decrease in BDE for a 9-Me_3SiCH_2 group in fluorene was only 3.7 kcal compared to 6.4 kcal for a Me_3CCH_2 group. This reversal is believed to be associated with the larger steric effect in 9-neopentylfluorene than in the Me_3SiCH_2 analogue. In conclusion, β-trimethylsilyl stabilizing effects on carbon-centered radicals can be as large as 4.5 kcal, but there is little β-silyl effect on carbanions.

Table 4. Summary of pK_{HA} Measurements[a]

acid	indicator (pK_{HIn})[b]	pK_{HA}	std
$CH_3C(S)OEt$	CNAH (18.9)	19.22	0.01
	FMY30 (18.1)	19.10	0.02
$CH_3CH_2C(S)OEt$	CNAH (18.9)	18.82	0.03
	PFH (17.9)	18.77	0.04
$CH_3CH_2CH_2C(S)OEt$	CNAH (18.9)	19.15	0.01
	PFH (17.9)	18.90	0.05
t-$BuCH_2CH_2C(S)OEt$	CNAH (18.9)	18.69	0.01
	PFH (17.9)	18.75	0.05
$Me_3SiCH_2CH_2C(S)OEt$	CNAH (18.9)	18.60	0.01
	PFH (17.9)	18.59	0.03
	FMY30 (18.1)	18.63	0.01
$Me_3SiCH_2CH(COOEt)_2$	FMY30 (18.1)	18.57	0.01
	CNAH (18.9)	18.65	0.02
$CH_3C(O)CH(CH_2SiMe_3)$-COOEt	MCLPHF (16.8)	15.84	0.05
	MCLPHF (16.8)	15.80	0.04
$CH_3C(O)CH(CH_2CH_3)$-COOEt	MCLPHF (16.8)	16.42	0.07
	MCLPHF (16.8)	16.41	0.05
$CH_3C(O)CH_2COOEt$	PSFH (15.4)	14.37	0.01
	FMY330 (13.8)	14.23	0.01
Me_3SiCH_2FlH	*m*-$FC_6H_4CH_2SO_2Ph$ (21.7)	21.31	0.02
(standard acid)	*m*-$CF_3C_6H_4CH_2SO_2Ph$ (21.7)	21.30	0.01

[a] Measured by the overlapping indicator method.[20] [b] Names of indicators: CNAH, 4-chloro-2-nitroaniline; FMY30, 2-(phenylsulfonyl)fluorene; PFH, 9-phenylfluorene; MCLDHF, 9-(*m*-chlorophenyl)fluorene; PSFH, 9-(phenylthio)fluorene.

Experimental Section

The pK_{HA} measurements in Me_2SO were carried out as described in earlier publications;[2] details are given in Table 4. Cyclic voltammetry was carried out in the manner previously described[18] using platinum working and auxiliary electrodes and a Ag/AgI reference electrode with 0.1 M $Et_4N^+BF_4^-$ electrolyte and ferrocene/ferrocenium as a standard. NMR spectra were recorded on a Varian GEMINI 300 or VRX 300.

Ethyl thionacetate $CH_3C(=S)OEt$, ethyl thionpropionate $CH_3CH_2C(=S)OEt$, and ethyl thionbutyrate $CH_3CH_2CH_2C(=S)OEt$ were prepared from the reaction of the appropriate ethyl ester with Lawesson's reagent (Aldrich).[12] A typical procedure is as follows.

Lawesson's reagent, 10 g, and an ethyl ester, 25 mL, were mixed in a 50 mL round-bottom flask. The two-phase mixture was refluxed, during which time aliquots were taken and analyzed by GLC, until the concentration of thionester failed to increase. This usually took about 2−4 days. The volatiles were transferred into another round-bottom flask under vacuum, leaving the solid materials behind. The thionester solution was then concentrated to 40−60% by fractional distillation, and the pure compound (>98%) was obtained by preparative GLC. The crude yield was between 30 and 50%.

Ethyl thionbutyrate $CH_3CH_2CH_2C(=S)OEt$ appears to be a new compound. Its spectroscopic data are as follows: ^1H NMR ($CDCl_3$) δ 0.942 (3H, t, CH_3), 1.386 (3H, t, CH_3), 1.758 (2H, hex, CH_2), 2.687 (2H, t, CH_2), 4.480 (2H, q, CH_2); mass spectrum *m/z* (relative abundance) 132 (100), 89 (25.3), 87 (29.4), 76 (39.2), 71 (76.9), 55 (31.5); high-resolution MS calcd for $C_6H_{12}OS$ 132.0609, found 132.0618.

Ethyl 3-(Trimethylsilyl)thionpropionate [$(Me_3Si)CH_2CH_2C(=S)OEt$]. Lawesson's reagent (1.2 g, 3 mmol, 6 mequiv of sulfur) and 0.8 g (4.6 mmol) of ethyl 3-(trimethylsilyl)-propionate, prepared according to the literature procedure,[19]

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were mixed in 30 mL of toluene. The mixture was refluxed for 3 days, and the final ratio of ester *vs* thionester was about 40:60, according to GLC analysis. The mixture was then passed through a silica gel column with methylene chloride as the elution solvent. The desired thionester was eluted first. The early fractions were combined and concentrated by removing most of the solvent. Ethyl 3-(trimethylsilyl)thionpropionate, 100 mg (11% yield), was obtained by preparative GLC (purity >98%): ^{1}H NMR ($CDCl_3$) δ 0.018 (9H, s, $Si(CH_3)_3$), 0.983 (2H, m, CH_2), 1.404 (3H, t, CH_3), 2.678 (2H, m, CH_2), 4.507 (2H, q, CH_2); mass spectrum *m/z* (relative abundance) 190 (1.9), 175 (68.2), 147 (41.4), 129 (17.0), 91 (29), 73 (100); high-resolution MS calcd for $C_8H_{18}OSSi$ 190.0848, found 190.0835.

Ethyl 3-*tert*-Butyl)propionate and Ethyl 3-*tert*-Butylthionpropionate. *tert*-Butylacetylene (25 g, 0.3 mol) and 300 mL of anhydrous Et_2O were placed in a 500 mL three-neck flask, and 120 mL of butyllithium (2.5 M in hexanes) was added dropwise at −78 °C. After stirring for 20 min, 30 g (0.28 mol) of ethyl chloroformate was added slowly. The solution was gradually warmed, and a white solid precipitated. The organic solution was separated from the solid, washed with 50 mL of H_2O, and then dried over anhydrous Na_2SO_4. After removal of the volatiles, distillation at 80 °C/0.8 mmHg yielded 40 g of ethyl 3-*tert*-butylpropynoate, $t\text{-BuC}{\equiv}\text{CC}(=\text{O})\text{OEt}$ (yield 81%). Hydrogenation of the ethyl 3-*tert*-butylpropynoate in ethanol with Pd/C catalyst gave a quantitative yield of ethyl 3-*tert*-butylpropionate, $t\text{-BuCH}_2\text{CH}_2\text{C}(=\text{O})\text{OEt}$. Refluxing the $t\text{-BuCH}_2\text{CH}_2\text{C}(=\text{O})\text{OEt}$ with Lawessen's reagent in toluene for 24 h produced ethyl 3-*tert*-butylthionpropionate (70% yield). A pure (>98%) sample was obtained by preparative GLC: ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 9H), 1.38 (t, 3H), 1.63 (m, 2H), 2.69 (m, 2H), 4.48 (q, 2H); high-resolution MS calcd for $C_9H_{18}OS$ 174.1078, found 174.1079.

9-((Trimethylsilyl)methyl)fluorene was prepared from the reaction of lithium fluorenide with (chloromethyl)trimethylsilane in THF and purified by recrystallization from ethanol. Colorless crystalline needles were obtained, and their ^{1}H NMR spectrum and mp were found to be identical to those reported by Bausch and Gong.[10] Repeated cyclic voltammetry experiments on the oxidation potential of 9-((trimethylsilyl)methyl)fluorenyl anion gave the $E_{ox}(A^-)$ value as shown in Table 2; the difference of the oxidation potentials between 9-((trimethylsilyl)methyl)fluorenyl anion and fluorenyl anion is 0.085 V, which is 0.135 V smaller than that reported earlier.[10]

Diethyl 2-((trimethylsilyl)methyl)malonate was prepared from the reaction of (trimethylsilyl)methyl chloride with diethyl malonate and pyridine in THF and purified by fractional distillation.

Ethyl 2-((trimethylsilyl)methyl)acetoacetate and ethyl 2-ethylacetoacetate were purchased from Aldrich and purified by fractional distillation.

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