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Regiochemical Control in the Preparation of 2-(Nosyloxy) β,γ-Unsaturated Esters and 4-(Nosyloxy) α,β-Unsaturated Esters from 1-[(Trimethylsilyl)oxy]-1-alkoxy 1,3-Dienes

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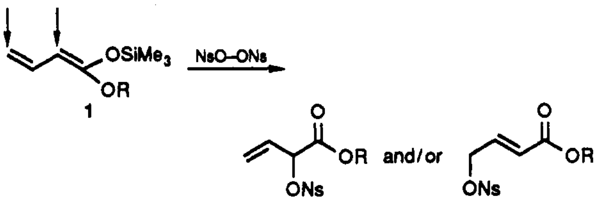
A series of 1-[(trialkylsilyl)oxy]-1-alkoxy 1,3-dienes **1a–i** were found to react with *p*-nitrobenzenesulfonyl peroxide in the presence of sodium methoxide or zinc chloride to give alkyl 2-[[(*p*-nitrophenyl)sulfonyl]oxy] β,γ-unsaturated esters **3** and alkyl 4-[[(*p*-nitrophenyl)sulfonyl]oxy] α,β-unsaturated esters **4** which are readily separable. The regioselectivity is determined by kinetic versus thermodynamic control. When positions 2 or 4 of the diene are unsubstituted, the 2-isomer is the major product and is the kinetically fastest formed product. It can be thermally rearranged to the more stable 4-isomer. When alkyl substituents are present at either the 2- or 4-positions, only the 4-isomer is obtained. Substitution for nosylate by amine nucleophiles occurs by an S_N2 process. Thus 2-amino β,γ-unsaturated esters and 4-amino α,β-unsaturated esters can be prepared from the appropriate starting nosylate.

Introduction

The introduction of nosylate leaving groups at the 2-position of ketones,[1] esters, and lactones,[2] dicarbonyl compounds including β-diketones and 3-keto esters,[3] and 3-keto amides[4] can be effected easily and in high yield by the electrophilic, oxidative addition of *p*-nitrobenzenesulfonyl peroxide (pNBSP) to enol derivatives of the corresponding carbonyl compounds. Sulfonyloxy groups can also be oxidatively attached to the 2-position of carbonyl compounds using hypervalent iodine reagents.[5,6] The versatility of 2-sulfonyloxy carbonyl compounds as synthetic intermediates has been amply demonstrated.[7]

We were thus attracted to the reaction of pNPSP with 1-[(trimethylsilyl)oxy]-1-alkoxy 1,3-dienes, **1**, since these conjugated silyl ketene acetals could give both α- and γ-addition products (eq 1). Both products would be very useful synthetic intermediates. By nucleophilic substitution for the nosylate group, the former offers an entry into β,γ-unsaturated esters and vinyl amino acids, the latter could be used to access γ-substituted α,β-unsaturated esters and γ-lactams.



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(1)

A priori, it is difficult to predict the preferred mode of addition of pNBSP to the conjugated ketene silyl acetal π-system of **1**. Various classes of electrophiles have been shown to exhibit different regiochemical preferences in their addition reactions with **1**.[8] In general carbon electrophiles,[9] halogen,[10] and pseudo halogens[11,12] give γ-attack nearly exclusively. Oxygen electrophiles are reported to give more α-attack but only few examples are known.[13] Steric features in the silyl dienolate also appear to be influential in determining the ratio of γ:α attack.[14]

Thus the addition of pNBSP to 1-(silyloxy)-1-alkoxy 1,3-dienes could not only give interesting and useful synthetic intermediates, it could also provide further insight into electrophilic additions to these activated dienes. We present results pertinent to both of these considerations.

Results

A series of 1-[(trimethylsilyl)oxy]-1-alkoxy 1,3-dienes **1a–f,h** were prepared from the corresponding α,β-unsaturated ester by conversion to the dienolate with LDA and trapping with TMSCl and HMPA,[11] or in the case of **1i** with TBDSCl. Compound **1g** was prepared by a similar sequence from methyl 2-methyl-3-butenoate. Kugelrohr distillation gave products which sometimes contained varying amounts of HMPA, but which were used effectively without further purification. Spectral properties of the silyl dienolates were indicative of the assigned structures. The products were sometimes formed as a mixture of *Z* and *E* isomers about the C1–C2 double bond. Several

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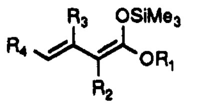
Table I. Product Yields from the Reaction of Diene 1b with Peroxide 2 in Ethyl Acetate

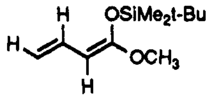
entry	conditions	yield (%)	ratio **3b**:**4b**
1	0 °C, CH_3ONa	73	1.2:1
2	−78 °C, CH_3ONa	100[a]	3:1
3	−78 °C, $ZnCl_2$	100[a]	3:1
4	−90 °C, $ZnCl_2$	100[a]	4:1

[a] Yield of crude product that was pure by ^1H NMR (>95%).

examples had been reported in the literature previously,[11] and ^1H NMR spectra for compounds not previously reported are given as supplementary material.

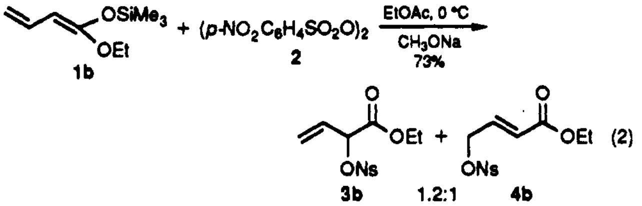


	R_1	R_2	R_3	R_4
1a	Me	H	H	H
1b	Et	H	H	H
1c	Et	H	Me	H
1d	t-Bu	H	Me	H
1e	Me	H	H	Me
1f	Me	H	H	Et
1g	Me	Me	H	H
1h	Et	H	Ph	H



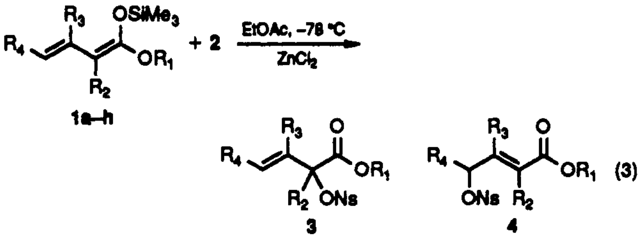
1i

Diene **1b**, used in exploratory studies to determine a suitable experimental protocol, was reacted with pNBSP, **2**, in ethyl acetate at 0 °C in the presence of 1 equiv of sodium methoxide suspended in the reaction mixture. The sodium methoxide was included to scavenge acidic byproducts which might be formed. (In work reported earlier we found that addition of an insoluble base to the reaction mixture was advantageous for substrates which tended to be acid sensitive,[3] so this procedure was followed in exploratory studies.) After 20 min, workup and flash chromatography[15] of the crude products delivered both the 2-nosyloxy ester, **3b**, and the 4-nosyloxy ester, **4b** (1.2:1), in 73% isolated yield (eq 2). When the reaction was carried out at −78 °C, the crude product isolated after a reaction time of 4 h (100%) was quite clean and contained a 3:1 ratio of **3b** to **4b** as determined by ^1H NMR.



A better procedure was found to be reaction of diene **1b** with **2** in ethyl acetate at −78 °C for 1 h in the presence of anhydrous zinc chloride (2 equiv) which also provided a quantitative yield of a virtually pure mixture of **3b** and **4b** (3:1). Lowering the reaction temperature to −90 °C increased the selectively to 4:1. Zinc chloride was used since this mild Lewis acid appears to form a complex with the sulfonyl peroxide **2** and increases its solubility in ethyl acetate markedly. (In the absence of any additive, longer reaction times are required by the slow solubility of **2** in the reaction mixture.) Zinc chloride may also increase the electrophilicity of **2**. The result is that sulfonyl peroxide additions proceed faster at lower temperatures in the presence of zinc chloride. The conjugated acetals **1** do not appear to be adversely affected by the presence of acid in the reaction mixture. These results are summarized in Table I.

Table II. Products from the Reaction of 1-[(Trimethylsilyl)oxy]-1-alkoxy 1,3-Dienes with pNBSP in Ethyl Acetate at −78 °C in the Presence of Zinc Chloride



entry	substrate[a]	yield (%)[b]	ratio **3**:**4**
1	**1a**: R_1 = Me	75	82:18
2	**1b**: R_1 = Et	73 (100)	77:23
3	**1c**: R_1 = Et; R_3 = Me	78[c]	64:36
4	**1d**: R_1 = *t*-Bu; R_3 = Me	(100)	0:100[e]
5	**1e**: R_1 = Me; R_4 = Me	68	0:100[e]
6	**1f**: R_1 = Me; R_4 = Et	43	0:100[d,e]
7	**1g**: R_1 = Me; R_2 = Me	71	0:100[e]
8	**1h**: R_1 = Et; R_3 = Ph	80	100:0[e]
9	**1i**: R_1 = Me; OSi(*t*-Bu)Me_2	81	72:28

[a] Only substituents other than hydrogen are noted. [b] Isolated yields of pure products. Yields in parentheses are crude yields for reactions where the crude products were of high purity by ^1H NMR. [c] Reaction carried out in the presence of $NaOCH_3$ (1 equiv). [d] This reaction was carried out at room temperature. [e] Only isomer detected by ^1H NMR.

These preliminary experiments established several important points. First, the addition of pNBSP to 1-[(trimethylsilyl)oxy]-1-alkoxy 1,3-dienes occurs smoothly to give allylic nosyloxy esters in high yields. Second, products of both α- and γ-attack are formed which are easily separable by chromatography. Third, α-attack on **1b** appears to be faster than γ-attack as is suggested by its predominance at low temperatures. Finally, similar results are obtained in the presence of either sodium methoxide or zinc chloride. For experimental convenience, zinc chloride is the additive of choice.

A series of silyloxy alkoxy dienes **1a–i** was reacted with **2** in ethyl acetate solution at −78 °C in the presence of 2 equiv of zinc chloride. In most cases the crude products were very clean and consisted of the 2-nosyloxy esters **3a–i** and/or the 4-nosyloxy esters **4a–i** along with trace amounts of the unsaturated esters from which **1a–i** were prepared. The regioisomers **3** and **4** were separable by flash chromatography[15] using hexane–ethyl acetate as the eluting solvent. Table II lists the results of these reactions.

The data in Table II reveal that the regiochemistry of the products obtained from the electrophile addition of pNBSP to **1** is heavily dependent on the substitution pattern of **1** and on the size of the ester alkoxy group of **1**. In those cases where only hydrogen substituents are present at C-2 and C-4 of the silyloxy diene (entries 1–3, 8, 9), the α-nosyloxy ester **3** is the major product. Substituents at C-3 have only small influence on the product partitioning as seen for R_3 = H (**1b**, entry 2), R_3 = Me (**1c**, entry 3), and R_3 = Ph (**1h**, entry 8). The addition regiochemistry is, however, very sensitive to steric bulk in the alkoxy group. Thus 3-methyl *O*-ethyldienolate **1c** gave a 1.8:1 ratio of **3c**:**4c** whereas 3-methyl *O*-*tert*-butyldienolate **1d** gave only **4d**. Evidently the bulky *tert*-butyl substituent precludes addition at the 2-position. Increasing bulk of the silyl group causes a similar, but much smaller change (compare entries 1 and 9). In cases where there are alkyl substituents at either C-2 or C-4, only the 4-nosyloxy product **4** is observed (entries 5–7).

It thus appeared for several cases that the 2-nosyloxy ester produced by electrophilic addition at the α-position

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Table III. Rearrangement of 3:4 Mixtures in Refluxing Toluene

entry	substrate[a]	starting α:γ	time[b]	yield (%)[c]	final α:γ
1	**3a**: R_1 = Me	82:18	36	80	0:100[d]
2	**3b**: R_1 = Et	77:23	24	100	0:100[d]
3	**3c**: R_1 = Et; R_3 = Me	67:33	72	100	8:92
4	**3h**: R_1 = Et; R_3 = Ph	100:0	72	dec	–

[a] Only substituents other than hydrogen are noted. [b] Time in hours. [c] Recovery yield. [d] Only isomer detected by ^{1}H NMR.

Table IV. Substitution Reactions of 2-Nosyloxy Esters 3 and 4-Nosyloxy Esters 4 with Amine Nucleophiles

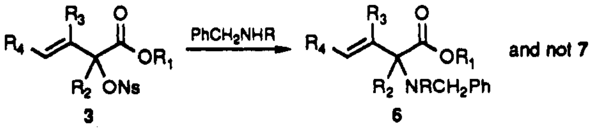
entry	reactant	amine	product	yield (%)[a]
1	**3a**	$PhCH_2NH_2$	**6a**	77[b]
2	**4a**	$PhCH_2NH_2$	**7a**	88
3	**3b**	$PhCH_2NH_2$	**6b**	91[c]
4	**4b**	$PhCH_2NH_2$	**7b**	96
5	**4c**	$PhCH_2NH_2$	**7c**	86
6	**4d**	$PhCH_2NH_2$	**7d**	63[d]
7	**4e**	$PhCH_2NH_2$	**73**	87
8	**4f**	$PhCH_2NH_2$	**7f**	52[d]
9	**4g**	$PhCH_2NHCH_3$	**7g** (R = CH_3)	88
10	**3h**	$PhCH_2NHCH_3$	**6h** (R = CH_3)	60[d]

[a] Isolated yields. [b] This result was obtained using a 80:20 mixture of **3a** and **4a**. [c] This result was obtained using a 81:19 mixture of **3b** and **4b**. [d] This was the yield of the two-step process from the 1-[(trimethylsilyl)oxy]-1-alkoxy 1,3-diene without purification of the nosyloxy intermediate.

was the kinetically favored product. In order to confirm this, the initially formed mixtures of **3** and **4** were refluxed in toluene. Gradual 1,3-rearrangement of the nosyloxy group from the 2- to the 4-position provided the 4-nosyloxy product in high yields. These results are shown in Table III.

The unsubstituted compounds rearranged smoothly to the 4-nosyloxy product in high yields (entries 1, 2). Substituents at the 3-position slow down the rearrangement significantly (entries 3, 4) to the extent that a 3-phenyl substituent gives only decomposition products and not rearranged product. The results indicate that the 4-nosyloxy ester is the thermodynamically most stable product. It follows that electrophilic attack of pNBSP at the 2-position of dienes **1a–c,h,i** is governed by kinetic factors. Thus either regioisomer can be obtained in good yields for those cases where the 1,3-rearrangement is observed.

The nosyloxy group in **3** and **4** is readily replaced by amine nucleophiles. Direct S_N2 replacement, and not S_N2' substitution, is found for both 2-nosyloxy and 4-nosyloxy isomers (eqs 4, 5). The results of substitution reactions are given in Table IV.



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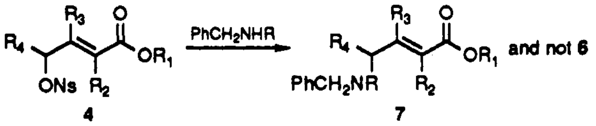


(5)

In general good yields of substitution products were obtained. The 2-nosyloxy esters **3a**, **3b**, and **3h** gave the 2-benzylamino products **6a**, **6b**, and **6h** in good yields; however, attempts to purify **6a** and **6b** (but not **6h**) by flash chromatography led to decomposition. The 4-nosyloxy esters **4a–g** gave only the 4-amino-substituted α,β-unsaturated esters **7** in good yields. In several cases where only the 4-nosyloxy ester was produced in the addition reaction, the crude product was reacted directly with the amine nucleophile to give the 4-amino unsaturated ester in a one-pot process (entries 6, 8, 10), also in good yields. With the expectation that other nucleophiles would react similarly, regiospecific preparations of 2-substituted β,γ-unsaturated esters and 4-substituted α,β-unsaturated esters can be achieved by this route.

Discussion

The regiochemistry of the addition of pNBSP to 1-[(trimethylsilyl)oxy]-1-alkoxy 1,3-dienes is sensitive to the substitution pattern of the diene and to steric effects therein. When positions 2 and 4 of the diene are unsubstituted, then the 2-nosyloxy product resulting from electrophilic attack at the α-position is favored kinetically. This kinetic preference is little affected by substituents at the 3-position of the diene. Steric bulk in the alkoxy group slows electrophilic attack at the 2-position, and the 4-nosyloxy product is produced. A less pronounced steric effect is observed for larger groups attached to silicon. Analogous changes in product regiochemistry have been observed in the addition of sulfonium ions to silyl dienolates, where it was found that increasing the bulk of substituents on silicon led to increasing amounts of γ-addition.[14] In the present case steric effects of the alkoxy substituent appear to be more influential, perhaps because of the larger size of the electrophile and because an alkoxy substituent is closer to C-2 than when it is part of a siloxy group. Several of the siloxy dienes **1** were *Z*/*E* mixtures; however, the influence of olefin geometry of the regiochemistry of the addition is unknown.

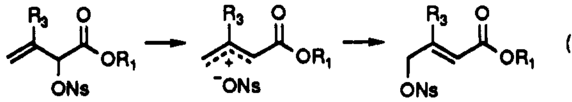
If alkyl substituents are present at either the 2- or 4-positions of the diene, only the 4-nosyloxy product is obtained. This product could result either from faster attack at the 4-position in these substrates, or it could result from rapid rearrangement of the kinetically favored 2-nosyloxy product to the thermodynamically more stable 4-substituted product. While no data is in hand that distinguishes these possibilities, at present we favor the latter explanation.

An alkyl substituent at the 4-position of the diene should have little influence on either the electron density or the steric congestion at the 2-position of the diene system. Thus dienes with 4-alkyl groups are predicted to show the same kinetic preference for α-attack as observed for unsubstituted dienes. Such is not the case.

Furthermore, the 1,3-rearrangement of the nosyl group appears to be very sensitive to substituents in the 2-nosyloxy ester. Whereas unsubstituted 2-nosyloxy esters **3a,b** rearrange completely in 24 h in refluxing toluene, the 3-methyl derivative **3c** takes more than 72 h for rearrangement, and the 3-phenyl derivative **3h** fails to give rearranged product under these conditions.

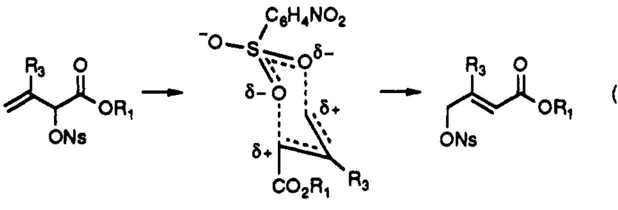
The 1,3-rearrangement of nosylate could occur by either an ion pair mechanism or by a concerted 3,3-type rearrangement. The effect of substituents at the 3-position on the rearrangement is more consistent with a concerted 3,3-rearrangement of sulfonate than with the formation and recombination of ion pairs. Placement of a methyl or phenyl group at the 3-position should have little influence on the stability of the allyl cation produced by ionization, and thus should have little influence on the rate of ionization and rearrangement (eq 6). In fact, substituents at the 3-position retard the rearrangement significantly.

On the other hand little precedence exists for the alternate 3,3-rearrangement pathway. While the 3,3-rear-



(6)

rangements of allylic esters[16] and xanthates[17] have been observed, we have been unable to find reports of 3,3-rearrangements of sulfonate esters in all carbon systems. Concerted 3,3-rearrangements of sulfonate groups from nitrogen to carbon in enamide systems are known to be facile, however.[18] Were such a pathway operative, however, it would likely have a chairlike transition state 8 as found in other Cope-type rearrangements,[18] and due to the leaving group properties of the rearranging nosyloxy group, the transition state is likely to have a significant amount of ionic character (eq 7).



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(7)

In this transition state for concerted rearrangement, the substituent at the 3-position (R_3) must occupy a pseudoaxial position. As the size of this group increases $H < CH_3 < C_6H_5$, the transition state is raised in energy and the rearrangement is retarded. This is the trend that is qualitatively observed. In the case where R_3 = Ph, the rearrangement is slowed to the point that other decomposition pathways, presumably ionic, dominate. It is also seen that alkyl substituents at the 2- or 4-positions would stabilize the polar transition state 8 and thus increase the rate of rearrangement. If the acceleration is large, the kinetically formed 2-nosyloxy product would rapidly isomerize to the thermodynamically favored 4-nosyloxy product, which is the sole product obtained when there are alkyl substituents at C-2 or C-4.

The facile substitution of the nosylate group by nucleophiles occurs readily when it is attached at either C-2 or C-4 of the unsaturated ester. Direct substitution, and not S_N2' displacement, affords substituted unsaturated ester products in high yields.

Experimental Section

Melting points are uncorrected. Thin-layer chromatography was performed on silica gel 60 F_{254} plates from and visualized by UV irradiation and/or iodine. Flash chromatography was performed using silica gel 60 (230–400 mesh). *p*-Nitrobenzenesulfonyl peroxide (pNBSP) was prepared by the literature method.[19]

1-[(Trimethylsilyl)oxy]-1-ethoxy-1,3-butadiene (1b) was prepared from ethyl crotonate by the following general method:[11] HMPA (*cancer suspect agent*, 4.0 mL) was added to a stirred, cooled (0 °C) solution of lithium diisopropylamide (22.0 mmol) in tetrahydrofuran (20 mL) under nitrogen. After the solution was cooled to −78 °C, ethyl crotonate (2.30 g, 20 mmol) was added and the mixture was stirred at −78 °C for 30 min. Trimethylsilyl chloride (4.0 mL) was added, and the reaction mixture was warmed to room temperature over 1 h. Most of tetrahydrofuran was removed by rotary evaporation to provide a white residue which was taken up in dry pentane (150 mL) and filtered through a glass-fritted filter. The filtrate was concentrated and distilled by bulb-to-bulb distillation (70 °C, 0.1 mmHg) to furnish **1b** as a colorless oil (2.80 g, 75%):[9b] NMR ($CDCl_3$) δ 0.19 (s, 9 H, $Si(CH_3)_3$), 1.26 (t, 3 H, J = 7.0 Hz, $\mathrm{CH_2C}H_3$), 3.76 (q, 2 H, J = 7.0 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 4.41 (d, 1 H, J = 10.4 Hz, *cis*-EtOC=C*H*), 4.53 (dd, 1 H, J = 10.5, 2.2 Hz, $\mathrm{CH{=}C}H_2$), 4.77 (dd, 1 H, J = 17.2, 2.2 Hz, $\mathrm{CH{=}C}H_2$), 6.47 (2 t, 1 H, J = 17.2, 10.5 Hz, $\mathrm{C}H\mathrm{{=}CH_2}$).

1-[(Trimethylsilyl)oxy]-1-methoxy-1,3-butadiene (1a) was prepared from methyl crotonate (2.0 g, 20 mmol), LDA (22 mmol), HMPA (4 mL), and trimethylsilyl chloride (4 mL) as a colorless oil (2.50 g, 73%) after purification by bulb-to-bulb distillation (70–80 °C, 0.1 mmHg): NMR ($CDCl_3$) δ 0.18 (s, 9 H, $Si(CH_3)_3$), 3.56 (s, 3 H, OCH_3), 4.48 (d, 1 H, J = 10.2 Hz, *cis*-MeOC=C*H*), 4.79 (dd, 1 H, J = 10.4, 2.2 Hz, $\mathrm{CH{=}C}H_2$), 4.88 (dd, 1 H, J = 17.0, 2.2 Hz, $\mathrm{CH{=}C}H_2$), 6.47 (2 t, 1 H, J = 17.2, 10.4 Hz, $\mathrm{C}H\mathrm{{=}CH_2}$).

1-[(Trimethylsilyl)oxy]-1-ethoxy-3-methyl-1,3-butadiene (1c) was prepared from ethyl β,β-dimethylacrylate (2.56 g, 20.0 mmol), LDA (25 mmol), HMPA (4 mL), and trimethylsilyl chloride (4 mL) as a colorless oil (2.93 g, 73%) after purification by bulb-to-bulb distillation (70–80 °C, 0.1 mmHg): NMR ($CDCl_3$) δ 0.20 (s, 9 H, $Si(CH_3)_3$), 1.26 (t, 3 H, J = 7.0 Hz, $\mathrm{CH_2C}H_3$), 1.89 (t, 3 H, J = 0.6 Hz, $\mathrm{CH_2{=}C(C}H_3\mathrm{))}$), 3.75 (q, 2 H, J = 7.0 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 4.19 (s, 1 H, EtOC=C*H*), 4.49 (m, 1 H, $\mathrm{C}H_2\mathrm{{=}C(CH_3)}$), 4.73 (m, 1 H, $\mathrm{C}H_2\mathrm{{=}C(CH_3)}$).

1-[(Trimethylsilyl)oxy]-1-*tert*-butoxy-3-methyl-1,3-butadiene (1d) was prepared from *tert*-butyl 3-methyl-2-butenoate (2.10 g, 13.5 mmol), LDA (15 mmol), HMPA (3 mL), and trimethylsilyl chloride (3 mL) as a colorless oil (2.63 g, 85%) after purification by bulb-to-bulb distillation as reported in the literature.[11]

1-[(Trimethylsilyl)oxy]-1-methoxy-1,3-pentadiene (1e) was prepared from *trans*-methyl 2-pentenoate (1.20 g, 10.5 mmol), LDA (13.0 mmol), HMPA (3.0 mL), and trimethylsilyl chloride (3.0 mL) as a colorless oil after bulb-to-bulb distillation (70–80 °C, 0.1 mmHg). The product was contaminated with HMPA. The yield of **1e** was 760 mg (41%):[20] NMR ($CDCl_3$) δ 0.19 (s, 9 H, $Si(CH_3)_3$), 1.65 (dd, 3 H, J = 6.8, 1.6 Hz, $\mathrm{CHC}H_3$), 3.58 (s, 3 H, OCH_3), 4.53 (d, 1 H, J = 10.8 Hz, *cis*-MeOC=C*H*), 5.07 (m, 1 H, $\mathrm{{=}C}H\mathrm{CH_3}$), 6.12 (m, 1 H, $\mathrm{C}H\mathrm{{=}CHCH_3}$).

1-[(Trimethylsilyl)oxy]-1-methoxy-1,3-hexadiene (1f) was prepared from *trans*-methyl 2-hexenoate (3.1 g, 25 mmol), LDA (30 mmol), HMPA (6 mL), and trimethylsilyl chloride (6 mL) as a colorless oil after bulb-to-bulb distillation (70–80 °C, 0.1 mmHg). The product was contaminated with HMPA. The yield of **1f** was 3.25 g (68%). The product contained *Z* and *E* isomers. The major isomer had NMR ($CDCl_3$) δ 0.18 (s, 9 H, $Si(CH_3)_3$), 1.03 (m, 3 H, $\mathrm{CH_2C}H_3$), 2.06 (m, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.55 (s, 3 H, OCH_3), 4.51 (dd, 1 H, J = 1, 10.8 Hz, *cis*-MeOC=C*H*), 4.98 (ddt, 1 H, J = 1, 7.2, 10 Hz, $\mathrm{{=}C}H\mathrm{CH_2CH_3}$), 6.04 (ddt, 1 H, J = 10, 10.8 Hz, *cis*-=$\mathrm{CHC}H\mathrm{{=}CHCH_2CH_3}$).

1-[(Trimethylsilyl)oxy]-1-methoxy-2-methyl-1,3-butadiene (1g) was prepared from methyl 2-methyl-3-butenoate (1.45 g, 12.7 mmol), LDA (14 mmol), and trimethylsilyl chloride (3 mL) as a colorless oil after bulb-to-bulb distillation (70–80 °C, 0.1 mmHg). This product was contaminated with HMPA. The yield of **1g** was 450 mg (15%). The material was a mixture of *Z* and *E* isomers and was used without further purification.

1-[(Trimethylsilyl)oxy]-1-ethoxy-3-phenyl-1,3-butadiene (1h) was prepared from ethyl 3-phenyl-2-butenoate (prepared by a Wittig–Horner reaction,[20] 1.14 g, 6.0 mmol), LDA (8.0 mmol), HMPA (2 mL), and trimethylsilyl chloride (2 mL) as a colorless oil after bulb-to-bulb distillation (70–80 °C, 0.1 mmHg). The product was contaminated with HMPA. The yield of **1h** was 1.31 g (83%): NMR ($CDCl_3$) δ 0.21 (s, 9 H, $Si(CH_3)_3$), 1.22 and 1.37 (2 t, 3 H, 3:1 ratio, J = 7.0 Hz, $\mathrm{OCH_2C}H_3$), 3.90 and 4.15 (2 q, 2 H, 3:1 ratio, J = 7.0 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.40 (s, 1 H, EtOC=C*H*), 5.12 and 5.29 (2 dd, 1 H, 3:1 ratio, J = 2.0 Hz, $\mathrm{C(Ph){=}C}H_2$), 5.39 and 5.58 (2 dd, 1 H, 3:1 ratio, J = 1.8 Hz, $\mathrm{C(Ph){=}C}H_2$), 7.40 (m, 5 H, phenyl). The product was a 3:1 ratio of *E*:*Z* isomers.

1-[(*tert*-Butyldimethylsilyl)oxy]-1-methoxy-1,3-butadiene (1i) was prepared from methyl crotonate (2.0 g, 20 mmol), LDA (22 mmol), HMPA (4.0 mL), and *tert*-butyldimethylsilyl chloride (3.8 g) as a colorless oil after bulb-to-bulb distillation (70–80 °C,

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0.1 mmHg). The product contained HMPA. The yield of **1i** was 3.86 g (81%): NMR ($CDCl_3$) δ 0.16 (s, 6 H, $Si(CH_3)_2$), 0.94 (s, 9 H, Si-*t*-Bu), 3.56 (s, 3 H, OCH_3), 4.46 (d, 1 H, *J* = 10.4 Hz, *cis*-MeOC=CH), 4.59 (dq, 1 H, *J* = 10.4, 2.0, 0.8 Hz, $CH=CH_2$), 4.83 (dq, 1 H, *J* = 17.8, 2.0, 0.8 Hz, $CH=CH_2$), 6.51 (dt, 1 H, *J* = 17.8, 10.4, $CH=CH_2$).

Methyl 2-[[(*p*-Nitrophenyl)sulfonyl]oxy]-3-butenoate (3a) and Methyl 4-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-butenoate (4a). A solution of 1-[(trimethylsilyl)oxy]-1-methoxy-1,3-butadiene (**1a**, 430 mg, 2.5 mmol) in ethyl acetate (20 mL) was added dropwise to a stirred solution of pNBSP (810 mg, 2.0 mmol) and $ZnCl_2$ (340 mg, 3.0 mmol) in ethyl acetate (60 mL) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 20 min, washed with brine (100 mL), passed through a short pad of $MgSO_4$ and silica gel 60, and concentrated to provide a pale yellow oil which was separated by flash chromatography (hexane–ethyl acetate, 90:10 to 80:20). **3a**: clear oil (160 mg, 27%); NMR ($CDCl_3$) δ 3.75 (s, 3 H, OCH_3), 5.43 (d, 1 H, *J* = 10.6 Hz, $CH=CH_2$), 5.46 (d, 1 H, *J* = 10.8 Hz, CHONs), 5.52 (d, 1 H, *J* = 16.8 Hz, $CH=CH_2$), 5.89 (m, 1 H, $CH=CH_2$), 8.15 and 8.40 (AB q, 4 H, *J* = 9 Hz, aromatic CH); FTIR (CH_2Cl_2) 3106, 2957, 1762, 1535, 1352, 1189 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_7S$: C, 43.85; H, 3.65; N, 4.65. Found: C, 43.68; 3.59; 4.26.

4a (180 mg, 30%): mp 80–83 °C; NMR ($CDCl_3$) δ 3.75 (s, 3 H, OCH_3), 4.84 (dd, 2 H, *J* = 2, 5 Hz, CH_2ONs), 6.08 (dd, 1 H, *J* = 1.6, 15.8 Hz, *trans*-$CH_3O_2CH=$), 6.86 (dt, 1 H, *J* = 4.8, 15.8 Hz, *trans*-$=CHCH_2ONs$), 8.10 and 8.40 (AB q, 4 H, *J* = 9 Hz, aromatic CH); FTIR (CH_2Cl_2) 3105, 2953, 1724, 1535, 1351, 1187 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_7S$: C, 43.85; H, 3.65; N, 4.65. Found: C, 43.80; H, 3.72; N, 4.14.

If the reaction was carried out at −78 °C for 1 h; a mixture of **3a** and **4a** in a ratio of 82:18 was obtained in 75% isolated yield.

By use of the same general procedure, 1-[(*tert*-butyldimethylsilyl)oxy]-1-methoxy-1,3-butadiene (**1i**, 3.0 mmol), pNBSP (1.21 g, 3.0 mmol), and $ZnCl_2$ (820 mg, 6.0 mmol) in ethyl acetate (60 mL) at −78 °C, a mixture of **3a** and **4a** (730 mg, 81%) in the ratio of 72:28 was obtained.

Ethyl 2-[[(*p*-Nitrophenyl)sulfonyl]oxy]-3-butenoate (3b) and Ethyl 4-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-butenoate (4b). Use of the same general procedure, 1-[(trimethylsilyl)oxy]-1-ethoxy-1,3-butadiene, **1b** (370 mg, 2.0 mmol), pNBSP (410 mg, 1 mmol), and $ZnCl_2$ (270 mg, 2.0 mmol) at −78 °C, gave a mixture of **3b** and **4b** which was separated by flash chromatography (hexane–ethyl acetate, 90:10). **3b** (250 mg, 40%); clear oil; NMR ($CDCl_3$) δ 1.25 (t, 3 H, *J* = 7 Hz, OCH_2CH_3), 4.19 (q, 2 H, *J* = 7 Hz, OCH_2CH_3), 5.43 (d, 1 H, *J* = 10.2 Hz, $CH=CH_2$), 5.45 (d, 1 H, *J* = 6.2 Hz, CHONs), 5.52 (d, 1 H, *J* = 17 Hz, $CH=CH_2$), 5.90 (dq, 1 H, *J* = 17, 10.2, 6.2 Hz, $CH=CH_2$), 8.16 and 8.42 (AB q, 4 H, *J* = 9 Hz, aromatic CH); FTIR (neat) 3108, 2986, 1756, 1534, 1372, 1352, 1189 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_7S$: C, 45.71; H, 4.13; N, 4.44. Found: C, 45.99; H, 4.11; N, 4.48.

4b (210 mg, 33%): white solid; mp 55–57 °C; NMR ($CDCl_3$) δ 1.28 (t, 3 H, *J* = 7 Hz, OCH_2CH_3), 4.19 (q, 2 H, *J* = 7 Hz, OCH_2CH_3), 4.82 (dd, 2 H, *J* = 1.7, 4.0 Hz, CH_2ONs), 6.06 (dt, 1 H, *J* = 1.7, 15.6 Hz, *trans*-$EtO_2CCH=$), 6.82 (dt, 1 H, *J* = 4.0, 15.6 Hz, *trans*-$CH=CHCH_2$), 8.15 and 8.44 (AB q, 4 H, *J* = 9 Hz, aromatic CH); FTIR ($CHCl_3$) 3107, 3025, 2985, 1719, 1530, 1370, 1187 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_7S$: C, 45.71; H, 4.13; N, 4.44. Found: C, 46.07; H, 4.21; N, 4.19.

The crude product (100%) was quite pure and contained **3b** and **4b** in a ratio of 77:23. Comparable results were obtained when sodium methoxide (110 mg, 1 mmol) was substituted for zinc chloride, but the yield decreased if the reaction was carried out at 0 °C.

Ethyl 3-Methyl-2-[[(*p*-nitrophenyl)sulfonyl]oxy]-3-butenoate (3c) and Ethyl 3-Methyl-4-[[(*p*-nitrophenyl)sulfonyl]oxy]-2-butenoate (4c). Use of the same general procedure, 1-[(trimethylsilyl)oxy]-1-ethoxy-3-methyl-1,3-butadiene, **1c** (600 mg, 3.0 mmol), pNBSP (810 mg, 2.0 mmol), and $NaOCH_3$ (170 mg) at −78 °C, gave a mixture of **3c** and **4c** (~78%) which was separated by flash chromatography (hexane–ethyl acetate, 90:10 to 70:30). **3c** could only be obtained as a mixture with **4c**. The NMR spectrum of **3c** was obtained from the mixture ($CDCl_3$) δ 1.25 (t, 3 H, *J* = 7 Hz, OCH_2CH_3), 1.73 (dd, 3 H, *J* = 0.8, 1.4 Hz, $CH_3C=CH_2$), 4.18 (q, 2 H, *J* = 7 Hz, OCH_2CH_3), 5.25 (set of m, 3 H, $CH_2=CCH_3$, CHONs), 8.18 and 8.39 (AB q, 4 H, *J* = 9 Hz, aromatic CH). Due to the inability to completely separate **3c**, elemental analysis was not obtained.

4c: colorless oil; NMR ($CDCl_3$) δ 1.27 (t, 3 H, *J* = 7 Hz, OCH_2CH_3), 2.08 (d, 3 H, *J* = 1.4 Hz, $CH_3C=CH$), 4.15 (q, 2 H, *J* = 7 Hz, OCH_2CH_3), 4.61 (d, 2 H, *J* = 1.2 Hz, CH_2ONs), 5.87 (q, 1 H, *J* = 1.2 Hz, $EtO_2CCH=$), 8.15 and 8.44 (AB q, 4 H, *J* = 9 Hz, aromatic CH); IR (neat) 3110, 2990, 1720, 1355, 1190 cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO_7S$: C, 47.42; H, 4.56; N, 4.26. Found: C, 47.31; H, 4.48; N, 4.29. The ratio of **3c** to **4c** in the crude product was found to be 64:36 by ^1H NMR analysis.

***tert*-Butyl 3-Methyl-4-[[(*p*-nitrophenyl)sulfonyl]oxy]-2-butenoate (4d).** Use of the same procedure, 1-[(trimethylsilyl)oxy]-1-(*tert*-butoxy)-3-methyl-1,3-butadiene, **1d** (910 mg, 4.0 mmol), pNBSP (810 mg, 2.0 mmol), and $ZnCl_2$ (550 mg, 4.0 mmol) in ethyl acetate (80 mL) at −78 °C, gave **4d** as a pale yellow oil in quantitative yield, which TLC showed to be nearly pure: NMR ($CDCl_3$) δ 1.39 (s, 9 H, $C(CH_3)_3$), 1.98 (s, 3 H, $CH_3C=$), 4.51 (s, 2 H, CH_2ONs), 5.72 (s, 1 H, $EtO_2CCH=$), 8.10 and 8.39 (AB q, 4 H, *J* = 9 Hz, aromatic CH); FTIR ($CHCl_3$) 3106, 3020, 2981, 1708, 1536, 1350, 1215, 1149 cm^{-1}.

Compound **4d** darkened at room temperature and was therefore used without further purification in subsequent reactions. Since elemental analysis was precluded by its instability, proof of structure for **4d** was accomplished by conversion to **4c**. The *tert*-butyl group of **4d** was removed with TFA (CH_2Cl_2, room temperature, 2 h) and the resulting acid was esterified with EtOH/DCC[21] to give **4c**, identical with an authentic sample.

Methyl 4-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-pentenoate (4e). Use of the same procedure, 1-[(trimethylsilyl)oxy]-1-methoxy-1,3-pentadiene, **1e** (1.35 mmol), pNBSP (810 mg, 2.0 mmol), and $ZnCl_2$ (420 mg, 3.0 mmol) in ethyl acetate (80 mL) at −78 °C, gave **4e** as a white solid (mp 55–56 °C, 290 mg, 68%) after purification by flash chromatography (hexane–ethyl acetate, 90:10 to 80:20) NMR ($CDCl_3$) δ 1.49 (d, 3 H, *J* = 6.6 Hz, $CHCH_3$), 3.73 (s, 3 H, OCH_3), 5.32 (dq, 1 H, *J* = 1.4, 6.6 Hz, CH_3CHONs), 5.94 (dd, 1 H, *J* = 1.4, 15.6 Hz, *trans*-$CH_3O_2CCH=$), 6.73 (dd, 1 H, *J* = 5.8, 15.6 Hz, *trans*-$CH=CHCHONs$), 8.12 and 8.42 (AB q, 4 H, *J* = 9 Hz, aromatic CH); FTIR ($CDCl_3$) 3106, 2988, 2953, 1727, 1536, 1351, 1188 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_7S{\cdot}H_2O$: C, 39.0; H, 5.1; N, 3.8. Found: C, 38.9; H, 4.6; N, 4.2.

Methyl 4-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-hexenoate (4f). Use of the same general procedure, 1-[(trimethylsilyl)oxy]-1-methoxy-1,3-hexadiene, **1f** (3.2 mmol), pNBSP (1.21 g, 3.0 mmol), and $ZnCl_2$ (550 mg, 4.0 mmol) in ethyl acetate (80 mL) at room temperature gave **4f** as a white solid (mp 73–76 °C, 420 mg, 43%) after purification by flash chromatography (hexane–ethyl acetate, 90:10 to 80:20): NMR ($CDCl_3$) δ 0.92 (t, 3 H, *J* = 7 Hz, $CHCH_2CH_3$), 1.78 (pentet, 2 H, *J* = 7 Hz, $CHCH_2CH_3$), 3.72 (s, 3 H, OCH_3), 5.14 (dq, 1 H, *J* = 1.2, 6.4 Hz, CHONs), 5.92 (dd, 1 H, *J* = 1.2, 15.8 Hz, *trans*-$CH_3O_2CCH=$), 6.69 (dd, 1 H, *J* = 6.4, 15.8 Hz, *trans*-$CH=CHCHONs$), 8.11 and 8.41 (AB q, 4 H, *J* = 9 Hz, aromatic CH); FTIR (CH_2Cl_2) 3106, 3060, 2986, 280, 1727, 1666, 1532, 1350, 1184 cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO_7S$: C, 47.42; H, 4.56; N, 4.26. Found: C, 47.26; H, 4.56; N, 4.16.

Methyl 2-Methyl-4-[[(*p*-nitrophenyl)sulfonyl]oxy]-2-butenoate (4g). Use of the same general procedure, 1-[(trimethylsilyl)oxy]-1-methoxy-2-methyl-1,3-butadiene, **1g** (2.0 mmol), pNBSP (1.21 g, 3.0 mmol), and $ZnCl_2$ (600 mg) in ethyl acetate (100 mL) at −78 °C, gave **4g** as a pale yellow oil (450 mg, 71%) after purification by flash chromatography (hexane–ethyl acetate, 95:5 to 80:20): NMR ($CDCl_3$) δ 1.85 (d, 3 H, *J* = 1.4 Hz, $CH_3O_2C(CH_3)=$), 3.74 (s, 3 H, OCH_3), 4.86 (dd, 2 H, *J* = 1.2, 6.6 Hz, CH_2ONs), 6.63 (dt, 1 H, *J* = 1.2, 6.6 Hz, $=CHCH_2ONs$), 8.14 and 8.43 (AB q, 4 H, *J* = 9 Hz, aromatic CH); FTIR ($CDCl_3$) 3106, 2954, 1720, 1535, 1350, 1187 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_7S{\cdot}H_2O$: C, 43.24; H, 4.54; N, 4.20. Found: C, 43.13; H, 4.77; N, 3.95.

Ethyl 2-[[(*p*-Nitrophenyl)sulfonyl]oxy]-3-phenyl-3-butenoate (3h). Use of the same general procedure, 1-[(trimethylsilyl)oxy]-1-ethoxy-3-phenyl-1,3-butadiene, **1h** (2.8 mmol), pNBSP (1.21 g, 3.0 mmol), and $ZnCl_2$ (900 mg, 6 mmol) in ethyl acetate (80 mL) at −78 °C, provided a brown oil (1.60 g). From

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[21] Neises, B.; Steglich, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 522.

the crude oil, 380 mg was purified by radial chromatography (hexane–ethyl acetate, 95:5) to give **3h** as pale yellow oil (210 mg, 80%): NMR ($CDCl_3$) δ 1.13 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 4.15 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 5.50 (d, 1 H, J = 0.6 Hz, $C(Ph){=}CH_2$), 5.63 (s, 1 H, $EtO_2CCH(ONs)$), 5.84 (d, 1 H, J = 0.6 Hz, $C(Ph){=}CH_2$), 7.27 (m, 5 H, phenyl), 8.04 and 8.29 (AB q, 4 H, J = 9 Hz, aromatic CH); FTIR ($CDCl_3$) 3106, 2984, 1753, 1535, 1350, 1187 cm^{-1}. Anal. Calcd for $C_{18}H_{17}NO_7S$: C, 55.24; H, 4.38; N, 3.58. Found: C, 55.06; H, 4.51; N, 3.33.

Methyl 2-(Benzylamino)-3-butenoate (6a) and Methyl 4-(Benzylamino)-2-butenoate (7a). The same general procedure for substitution reactions was employed. To a stirred solution of an 80:20 mixture of **3a** and **4a** (610 g, 2.0 mmol) in dichloromethane (50 mL) at 0 °C was added benzylamine (0.5 mL). After stirring at room temperature for 24 h, the reaction mixture was concentrated under reduced pressure. The residue was taken up in ethyl acetate (50 mL), washed with H_2O (50 mL), passed through a short pad of $MgSO_4$ and silica gel 60, and concentrated to provide an yellow oil (350 mg, 85%). Spectral analysis revealed that there was a 73:27 ratio of **6a**:**7a** in the crude product. However, attempts to separate this mixture by flash chromatography led to decomposition of the sample. The ^1H NMR spectra of each isomer was determined from the crude mixture. **6a**: NMR ($CDCl_3$) δ 3.77 (s and AB q, 5 H, J = 12 Hz for AB q, OCH_3 and $NHCH_2Ph$), 3.86 (d, 1 H, J = 6.8 Hz, $CHNHCH_2Ph$), 5.33 (2 dd, 2 H, J = 18, 11.2 Hz, $CH{=}CH_2$), 5.84 (m, 1 H, $CH{=}CH_2$), 7.34 (m, 5 H, phenyl). **7a**: δ 3.46 (d, 2 H, J = 6 Hz, CH_2NHCH_2Ph), 3.77 (s and AB q, 5 H, J = 12 Hz for AB q, OCH_3 and $NHCH_2Ph$), 6.05 (d, 1 H, J = 16 Hz, *trans*-$CH_3O_2CCH{=}$), 7.00 (m, 1 H, J = 6, 16 Hz, $CH{=}CHCH_2$), 7.34 (m, 5 H, phenyl).

Ethyl 2-(benzylamino)-3-butenoate (6b) and ethyl 4-(benzylamino)-2-butenoate (7b) were prepared from an 81:19 mixture of **3b** and –4b (330 mg, 1.0 mmol) and benzylamine (0.3 mL, 2.8 mmol) in dichloromethane (30 mL) at room temperature overnight. A mixture of **6b** and **7b** was obtained as a yellow oil (210 mg, 96%). NMR analysis of the crude product showed a 77:23 ratio of **6b**:**7b**. However, attempts to separate this mixture led to decomposition of the sample. The ^1H NMR spectra for each isomer was determined from the mixture, **6b**: NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7 Hz, OCH_2CH_3), 3.76 (s, 2 H, $NHCH_2Ph$), 3.85 (d, 1 H, J = 6.6 Hz, $CHNHCH_2Ph$), 4.19 (q, 2 H, J = 7 Hz, OCH_2CH_3), 5.30 (2 dd, 2 H, J = 17.2, 10.2 Hz, $CH{=}CH_2$), 5.85 (m, 1 H, J = 6.6, 10.2 Hz, $CH{=}CH_2$), 7.31 (m, 5 H, phenyl). **7b**: δ 1.27 (t, 3 H, J = 7 Hz, OCH_2CH_3), 3.40 (dd, 2 H, J = 5.2, 1.4 Hz, CH_2NHCH_2Ph), 3.79 (s, 2 H, $NHCH_2Ph$), 5.97 (m, 1 H, $EtO_2CCH{=}$), 7.01 (m, 1 H, $CH{=}CHCH_2$), 7.31 (m, 5 H, phenyl).

Ethyl 4-(Benzylamino)-3-methyl-2-butenoate (7c). A mixture of **3c** and **4c** (720 mg, 2.2 mmol, ratio 8:92) and benzylamine (0.6 mL) in dichloromethane (30 mL) at room temperature provided **7c** as a pale yellow oil (440 mg, 86%) after purification by flash chromatography (hexane–ethyl acetate, 80:20): NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7 Hz, CH_2CH_3), 2.15 (s, 3 H, $=CCH_3$), 3.27 (s, 2 H, CH_2NHCH_2Ph), 3.76 (s, 2 H, CH_2NHCH_2Ph), 4.16 (q, 2 H, J = 7 Hz, CH_2CH_3), 5.01 (s, 1 H, $EtO_2CCH{=}$), 7.34 (s, 5 H, phenyl); IR (neat) 3330, 3015, 2970, 1710, 1645, 1445 cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.10; H, 8.15; N, 6.00. Found: C, 71.89; H, 8.26; N, 5.76.

***tert*-Butyl 4-(Benzylamino)-3-methyl-2-butenoate (7d).** A solution of **4d** (prepared from **1d** and used without purification) and benzylamine (0.7 mL) in dichloromethane (50 mL) at room temperature overnight gave **7d** as a pale yellow oil (330 mg, 63% for two steps based on pNBSP) after purification by flash chromatography (hexane–ethyl acetate, 95:5 to 80:20): NMR ($CDCl_3$) δ 1.48 (s, 9 H, $C(CH_3)_3$), 2.12 (d, 3 H, J = 1.2 Hz, $CH{=}CCH_3$), 3.26 (d, 2 H, J = 1.2 Hz, $NHCH_2C{=}$), 3.76 (s, 2 H, $NHCH_2Ph$), 5.85 (t, 1 H, J = 1.2 Hz, $t\text{-}BuO_2CCH{=}$), 7.32 (s and m, phenyl and NH); IR (neat) 3330, 3050, 2960, 1700, 1645 cm^{-1}. Anal. Calcd for $C_{16}H_{23}NO_2{\cdot}{}^1/_4H_2O$: C, 72.32; H, 8.85; N, 5.27. Found: C, 72.56; H, 8.80; N, 5.66.

Methyl 4-(Benzylamino)-2-pentenoate (7e). A mixture of **4e** (140 mg, 0.44 mmol) and benzylamine (0.2 mL) in dichloromethane (15 mL) was stirred at room temperature for 3 days to give **7e** as a yellow oil (85 mg, 87%). TLC showed the crude product to be essentially pure, but an analytical samples was obtained by preparative TLC: NMR ($CDCl_3$) δ 1.21 (d, 3 H, J = 6.8 Hz, $CHCH_3$), 3.38 (m, 1 H, $CHNHBn$), 3.72 (AB q, 2 H, J = 12 Hz, $NHCH_2Ph$), 3.74 (s, 3 H, OCH_3), 5.95 (dd, 1 H, J = 15.8, 0.8 Hz, *trans*-$CH_3O_2CH{=}$), 6.85 (dd, 1 H, J = 15.8, 7.4 Hz, $CH{=}CHCHNHBn$), 7.30 (s, 5 H, phenyl); IR ($CHCl_3$) 3320, 3020, 2960, 1715, 1650 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO_2{\cdot}{}^1/_8H_2O$: C, 70.66; N, 6.22. Found: C, 70.48; H, 7.85; N, 6.32.

Methyl 4-(Benzylamino)-2-hexanoate (7f). A stirred solution of **4f** (which was prepared from **1f** (4.0 mmol) and pNBSP (3.0 mmol) and used without purification) and benzylamine (0.8 mL) in dichloromethane (50 mL) at room temperature provided **7f** as a pale yellow oil (360 mg, 52% for two steps) after purification by flash chromatography (hexane–ethyl acetate, 90:10 to 80:20): NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.4 Hz, CH_2CH_3), 1.55 (dq, 2 H, J = 7.4, 1.4 Hz, CH_2CH_3), 1.85 (br s, 1 H, NH), 3.13 (q, 1 H, J = 6.8 Hz, $CHNHCH_2Ph$), 3.70 (AB q, 2 H, J = 13.4 Hz, $NHCH_2Ph$), 3.75 (s, 3 H, OCH_3), 5.94 (d, 1 H, J = 15.8 Hz, $CH_3O_2CCH{=}$), 6.78 (dd, 1 H, J = 6.8, 15.8 Hz, $CH{=}CHCHNHCH_2Ph$), 7.30 (s, 5 H, phenyl); FTIR ($CDCl_3$) 3025, 2966, 1719, 1654, 1531, 1437 cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.10; H, 8.15; N, 6.01. Found: C, 72.08; H, 8.19; N, 5.78.

Methyl 2-Methyl-4-(*N*-methyl-*N*-benzylamino)-2-butenoate (7g). A mixture of **4g** (150 mg, 0.47 mmol) and *N*-methylbenzylamine (0.2 mL) in acetonitrile (50 mL) was heated at reflux overnight. Standard workup provided **7g** as a pale yellow oil (95 mg, 88%) after purification by preparative TLC (hexane–ethyl acetate, 90:10): NMR ($CDCl_3$) δ 1.83 (d, 3 H, J = 1.0 Hz, $CH_3O_2CC(CH_3){=}$), 2.23 (s, 3 H, NCH_3), 3.16 (dd, 2 H, J = 1.0, 6.6 Hz, $=CCH_2NCH_2Ph$), 3.52 (s, 2 H, NCH_2Ph), 3.75 (s, 3 H, OCH_3), 6.89 (dt, 1 H, J = 1.4, 6.6 Hz, $=CH$), 7.32 (m, 5 H, phenyl); FTIR ($CDCl_3$) 3029, 2962, 1713, 1624, 1526, 1436, 1260 cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO_2{\cdot}{}^1/_4H_2O$: C, 70.71; H, 8.48; N, 5.89. Found: C, 70.97; H, 8.38; N, 5.96.

Ethyl 2-(*N*-Methyl-*N*-benzylamino)-3-phenyl-3-butenoate (6h). A mixture of **3h**, which was prepared from the reaction of **1h** (3.7 mmol) and pNBSP (1.21 g, 3.0 mmol) and used without purification, and *N*-methylbenzylamine (1.0 mL) in acetonitrile (50 mL) was heated at reflux for 20 h. Standard workup gave **6h** as a pale yellow oil (560 mg, 60% for two steps) after purification by flash chromatography (hexane–ethyl acetate, 100:0 to 95:5): NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7.2 Hz, OCH_2CH_3), 2.32 (s, 3 H, NCH_3), 3.75 (AB q, 2 H, J = 13 Hz, NCH_2Ph), 4.22 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 4.45 (s, 1 H, EtO_2CCH), 5.37 (s, 1 H, $C(Ph){=}CH_2$), 5.59 (s, 1 H, $C(Ph){=}CH_2$), 7.1–7.5 (m, 10 H, phenyl); FTIR ($CDCl_3$) 3061, 2978, 1729, 1453 cm^{-1}. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.46; H, 7.49; N, 4.33.

Methyl 4-[[(*p*-Nitrophenyl)sulfonyl]oxy]-2-butenoate (4a) by Rearrangement of 3a. A crude mixture of **3a** and **4a** (ratio 82:18) obtained from the reaction of **1a** and pNBSP (2.0 mmol) was dissolved in toluene (80 mL) and heated at reflux for 36 h. After concentration of the solution under reduced pressure, the residue was purified by flash chromatography (hexane–ethyl acetate, 90:10) to provide **4a** (480 mg, 80%). The same procedure was used for the thermal rearrangements of **3b**, **3c**, and **3h**.

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Supplementary Material Available: ^1H NMR spectra of compounds **1a–i** (9 pages). Ordering information is given on any current masthead page.