mL), stirring the resulting mixture at room temperature for 1 h, and removing the solvent in vacuo. To a solution of the white salt in methanol (8 mL) was added a buffered $TiCl_3$ solution [NH_4OAc (7.40 g, 96 mmol) in H_2O (24 mL), 20% aqueous $TiCl_3$ (2.48 g, 16 mmol, 12.8 mL of H_2O)]. The reaction mixture was stirred at room temperature for 6 h and then poured into ether (50 mL). The aqueous phase was extracted with ether (2 × 50 mL). The organic extracts were combined, washed with 5% $NaHCO_3$ (50 mL) and brine (50 mL), and dried over $MgSO_4$, and the solvent was removed in vacuo. Kugelrohr distillation (105 °C/12.5 torr) of the resulting oil gave 0.35 g (80%) of **61** as a colorless oil.

61: IR (neat) 1665, 1615 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.74 (br, 1 H), 2.71–2.40 (m, 4 H), 2.32 (s, 3 H), 2.11–1.66 (br m, 2 H). Anal. ($C_7H_{10}O$) C, H.

Isomerization of 2-Nitro-2-nonene (77) into (*E*)-2-Nitro-3-nonene (78). A solution of **77** (1.71 g, 10 mmol) and **1** (0.88 g, 1.0 mmol) in benzene (25 mL) was refluxed for 24 h. The benzene solution was cooled, washed with aqueous 2 N HCl solution (10 mL) and water (10 mL), dried over $MgSO_4$, and concentrated in vacuo. Distillation of the resulting oil (74 °C/0.10 torr) gave 1.50 g (88%) of a mixture containing 57% of **77** and 43% of **78** determined by ^1H NMR integration of the olefin proton signal at δ 7.12 and the nitromethine proton signal at δ 4.99, respectively.

78: ^1H NMR (90 MHz, $CDCl_3$) δ 5.90 (dt, J = 14.9, 5.9 Hz, 1 H), 5.60 (dd, J = 14.9, 6.4 Hz, 1 H), 4.99 (dq, J = 6.4, 6.6 Hz, 1 H), 2.16 (m, 2 H), 1.60 (d, J = 6.6 Hz, 3 H), 1.49–1.04 (br m, 6 H), 0.89 (t, J = 5.3 Hz, 3 H).

Condensation of *n*-Heptanal with 5. In a round-bottomed flask fitted with a Dean and Stark trap were placed *n*-heptanal (2.28 g, 20 mmol), **5** (6.0 g, 80 mmol), **1** (0.53 g, 6.0 mmol), and benzene (50 mL), and the solution was refluxed for 1 h. The benzene solution was cooled, washed with aqueous 2 N HCl solution (20 mL) and water (20 mL), dried over $MgSO_4$, and concentrated in vacuo. Distillation of the resulting oil (74 °C/0.10 torr) gave 1.53 g (45%) of a mixture containing 72% of **77** and 28% of **78**.

Registry No. **1**, 108-00-9; **2**, 96-22-0; **3**, 75-52-5; (*E*)-**4**, 104488-74-6; (*Z*)-**4**, 104488-75-7; **5**, 79-24-3; (*E*)-**6**, 104488-76-8; (*Z*)-**6**, 104488-77-9; **7**, 565-69-5; (*E*)-**8**, 104488-78-0; (*Z*)-**8**, 104488-79-1; **9**, 108-10-1; (*E*)-**10**, 104488-80-4; (*Z*)-**10**, 104488-81-5; **11**, 107-87-9; (*E*)-**12**, 104488-82-6; (*Z*)-**12**, 104488-83-7; (*E*)-**13**, 104488-84-8; (*Z*)-**13**, 104488-85-9; **14**, 111-13-7; (*E*)-**15**, 104488-86-0; (*Z*)-**15**, 104488-87-1; **16**, 110-12-3; (*E*)-**17**, 104488-88-2; (*Z*)-**17**, 104488-89-3; **18**, 13984-50-4; (*E*)-**19**, 104488-90-6; (*Z*)-**19**, 104488-91-7; **20**, 93-55-0; (*E*)-**21**, 104488-92-8; (*Z*)-**21**, 104488-93-9; **22**, 98-86-2; **23**, 104488-94-0; **24**, 123-54-6; **25**, 104488-95-1; **26**, 105-45-3; **27**, 104488-96-2; **28**, 110-13-4; **29**, 31962-44-4; **30**, 120-92-3; **31**, 2562-42-7; **32**, 98810-07-2; **33**, 104488-97-3; **34**, 83-33-0; **35**, 1120-72-5; **36**, 104488-98-4; **37**, 104488-99-5; **38**, 108-94-1; **39**, 5330-61-0; **40**, 90087-64-2; **41**, 90942-72-6; **42**, 583-60-8; **43**, 104489-00-1; **44** (isomer 1), 104489-01-2; **44** (isomer 2), 104489-12-5; **45**, 591-24-2; **46**, 104489-02-3; **47**, 104489-03-4; **48**, 529-34-0; **49**, 104489-04-5; **50**, 502-42-1; **51**, 52315-51-2; **52**, 104489-05-6; **53**, 104489-06-7; **54**, 502-49-8; **55**, 104489-07-8; **56**, 104489-08-9; **57**, 104489-09-0; **58**, 830-13-7; (*E*)-**59**, 104489-10-3; (*Z*)-**59**, 104505-58-0; (*E*)-**60**, 104489-11-4; (*Z*)-**60**, 104505-59-1; **61**, 16112-10-0; **62**, 932-66-1; **63**, 41437-90-5; **64**, 14377-11-8; **65**, 96308-48-4; **66**, 60727-70-0; **67**, 35721-53-0; **68**, 49576-57-0; **69**, 54075-10-4; **77**, 4812-25-3; **78**, 104489-13-6; *n*-$C_3H_7NO_2$, 108-03-2; *n*-heptanal, 111-71-7.

Palladium-Catalyzed Substitutions of Allylic Nitro Compounds. Regiochemistry

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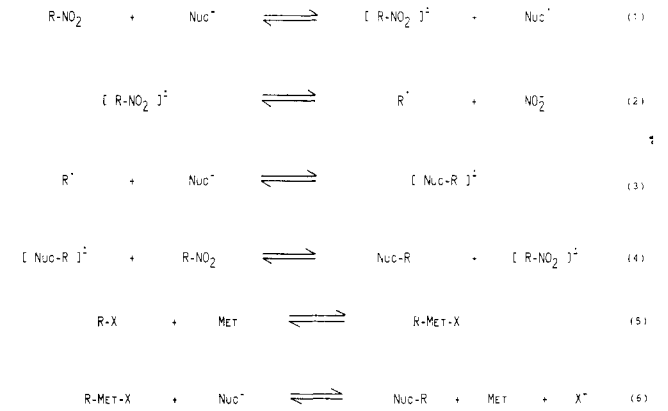
Primary, secondary, and tertiary allylic nitro compounds underwent Pd(0)-catalyzed allylic substitution by stabilized carbanions, secondary amines, and benzenesulfinate ion ($PhSO_2^-$). α,β-Disubstituted α-nitro olefins also behaved as allylic nitro compounds, via base-catalyzed vinyl → allyl rearrangement, and underwent allylic substitution by secondary amines and $PhSO_2^-$. The regiochemistry of these substitutions was dependent on the structure of the allylic nitro compound and on the steric bulk of the nucleophile. Generally, substitution occurred at the less hindered or least substituted site. In some cases added or generated $NaNO_2$ affected the regioselectivity of the allylic substitution of allylic nitro compounds and some allylic acetates by $PhSO_2^-$. Under these conditions, the more sterically hindered allylic sulfones were formed.

Over the last 2 decades, the $S_{RN}1$-type of substitution reaction of nitro compounds, which proceeds by an electron-transfer chain process involving radical anions and free radicals as intermediates, has been intensively studied by Kornblum and Russell and their co-workers.[3]

The mechanism of the $S_{RN}1$ reaction (eq 1–4) has some similarity to the general reaction mechanism of transition-metal-catalyzed substitution reactions (eq 5 and 6):[4]



the initial electron-transfer step followed by the formation

(1) Preliminary communications: (a) Tamura, R.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 3727–3729. (b) Tamura, R.; Hayashi, K.; Kai, Y.; Oda, D. *Tetrahedron Lett.* **1984**, *25*, 4437–4440. (c) Tamura, R.; Hayashi, K.; Kakihana, M.; Tsuji, M.; Oda, D. *Chem. Lett.* **1985**, 229–232. (d) Reference 2.

(2) Tamura, R.; Hayashi, K.; Kakihana, M.; Tsuji, M.; Oda, D. *Tetrahedron Lett.* **1985**, *26*, 851–854.

(3) For reviews, see: (a) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734–745. (b) Kornblum, N. In *Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*; Patai, S., Ed.; Wiley: New York, 1982; Part 1, pp 361–393.

0022-3263/86/1951-4375$01.50/0

Table I. Palladium-Catalyzed Allylic Alkylation and Amination of Tertiary Allylic Nitro Compounds[a]

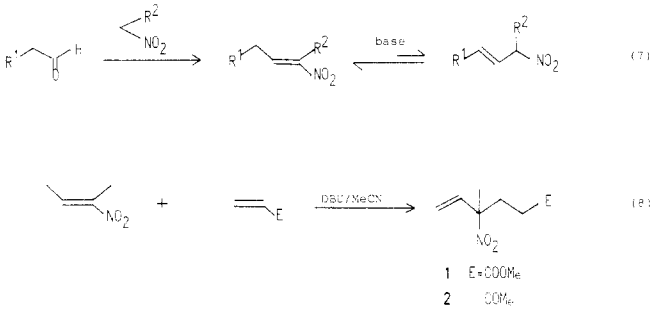
entry	nucleophile	nitro compound	solvent	time, h/temp, °C	product (E/Z)[b]	yield, %[c]
1	3	1	THF	6/65	**7a** + **8a** (80/20) 40:60[b]	52
2		1	DMF	6/70	**7a** + **8a** (*E*) 13:87[b]	66
3	4	1	DMF	20/25	**8b** (*E*)	64
4		2	DMF	20/25	**8c** (*E*)	61
5	5	1	CH_3CN	10/80	**7d** + **8d** (87/13) 47:53[b]	97
6	6	1	CH_3CN	10/80	**8e** (88/12)	74
7		1	THF	24/65	**8e** (–)[d]	17
8		2	CH_3CN	10/80	**8f** (83/17)	71

[a] Reactions were carried out with 1 mol % of $Pd(PPh_3)_4$ and 2 mol % of PPh_3. [b] Determined by ^1H NMR and GLC. [c] Isolated yield. [d] Undetermined.

of free radical (eq 1 and 2) and the coupling and subsequent electron-transfer steps (eq 3 and 4) in $S_{RN}1$ reaction correspond to the oxidative addition (eq 5) and the coupling step (eq 6) in transition-metal-mediated reaction, respectively. Furthermore, the former is a chain reaction and the latter is catalytic with respect to metal, which acts as the "chain carrier". This assumption prompted us to attempt the utilization of transition-metal catalysts for nitro compound chemistry.

Among the transition-metal-mediated substitution reactions, noteworthy is that of (π-allyl)palladium complexes, an area which has been extensively studied and applied to a variety of allylic substrates.[5,6] It is well-known that a nitro group in nitro paraffins accepts an electron and the resulting anion radical subsequently dissociates into nitrite ion (NO_2^-) and carbon free radical (eq 2).[3] We anticipated that this propensity might make the oxidative addition of allylic nitro compounds to palladium(0) possible, since oxidative addition to metal may be viewed as a sort of electron-transfer reaction. Indeed, we have found that allylic nitro compounds serve as excellent substrates for Pd(0)-catalyzed allylic substitution by nucleophiles.[1,2,7]

Initially, the utility of this process was limited by the lack of a general synthetic approach to the requisite allylic nitro compounds.[8] Our discovery that readily available α-nitro olefins could serve as an allylic nitro compound equivalent by the action of a base (eq 7 and 8), coupled

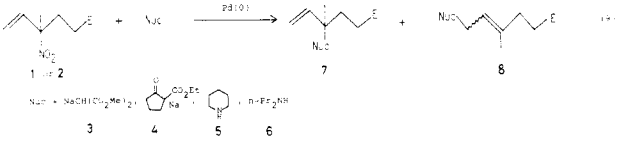


with our discovery that allylic nitro compounds are directly available from alicyclic and even aliphatic ketones and nitroalkanes (see previous paper), made allylic nitro compounds readily available as substrates for Pd(0)-catalyzed allylic substitution reactions.

In this paper, we report full experimental data for the Pd(0)-catalyzed substitution of the nitro group in various allylic nitro substrates by stabilized carbanions, amines, and benzenesulfinate ion ($PhSO_2^-$). The regioselectivity of attack by these nucleophiles on the allylic unit, as well as the effect of added $NaNO_2$ on the regiochemistry of the allylic substitution of allylic nitro compounds by $PhSO_2^-$, is also presented.

Results and Discussion

Alkylation and Amination. An important consideration in allylation with (π-allyl)palladium electrophiles is the control of the regiochemistry of attack by nucleophile on the allylic unit.[5] Inital studies centered on the regiocontrolled alkylation of the anion of nitroalkanes with tertiary allylic nitro compounds **1** and **2**. It is reported that tertiary nitroalkanes undergo substitution at the carbon bearing the nitro group by the anion of nitromethane via $S_{RN}1$ mechanism to give primary nitroalkanes having quaternary carbon center,[9] while the anion of nitroalkanes was alkylated by allylic acetates in the presence of Pd(0) catalyst predominantly at the least substituted site.[10] Thus it was assumed that the regiocontrolled alkylation of the anion of nitroalkanes with tertiary allylic nitro compounds **1** and **2** should be possible using Pd(0) catalysts or $S_{RN}1$ reaction conditions. However, all our attempts to use the anion of nitroalkanes as the nucleophile proved unsuccessful, giving no substitution product in both cases. Consequently, other stabilized carbanions such as malonic ester and β-keto esters were studied in an attempt to achieve regioselective allylation. Reactions of **1** or **2** with carbon nucleophiles were carried out in the presence of 1% $Pd(PPh_3)_4$ and an additional 2% PPh_3 (eq 9). As shown



in Table I, in the reaction with dimethyl sodiomalonate (**3**), DMF was a better solvent than THF with respect to both the yield and the regioselectivity. Changing **3** to the sterically encumbered sodio-2-carboethoxycyclopentanone (**4**) led to the exclusive attack at the less substituted terminus and gave the *E* isomer with high stereoselectivity.[11]

(4) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; pp 372–441.
(5) For reviews, see: (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615–2649. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1980. (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385–393. (d) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 8, pp 802–834.
(6) (a) Trost, B. M. *J. Org. Chem.* **1984**, *49*, 468–473. (b) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523–1529, and references therein.
(7) (a) Ono, N.; Hamamoto, I.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1982**, 821–822. (b) Ono, N.; Hamamoto, I.; Yanai, T.; Kaji, A. *Ibid.* **1985**, 523–524. (c) Ono, N.; Hamamoto, I.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1863–1864. (d) Ono, N.; Hamamoto, I.; Kaji, A. *Synthesis* **1985**, 950–952.
(8) See previous paper.
(9) Kornblum, N.; Erickson, A. S. *J. Org. Chem.* **1981**, *46*, 1039–1041.
(10) Wade, P. A.; Morrow, S. D.; Hardinger, S. A. *J. Org. Chem.* **1982**, *47*, 365–367.

Table II. Palladium-Catalyzed Allylic Alkylation and Amination of Cyclic Allylic Nitro Compounds

entry	nucleophile	nitro compound (*n*, R)	catalyst[a]	time, h/temp, °C	product	yield, %[b]
1	**3**	**9a** (1, H)	A	3/70	**14a**	70
2		**9b** (1, Me)	B	24/70	**14b**	61
3		**10a** (2, H)	B	24/70	**14c + 15c** 79:21[c]	64
4		**10b** (2, Me)	B	24/70	**14d + 15d** 65:35[c]	65
5		**11a** (3, H)	A	18/70	**14e**	71
6		**11b** (3, Me)	B	24/70	**14f**	56
7		**12a** (4, H)	B	24/70	**14g**	65
8		**12b** (4, Me)	B	24/70		0
9		**13** (8, H) (*E*/*Z* = 73/27)	B	24/70	**14h**[d]	68
10	**4**	**10a**	B	24/25	**14i**	52
11	**5**	**9a**	A	10/80	**14j**	85
12		**9b**	A	10/80	**14k**	75
13		**10a**	A	10/80	**14l + 15l** 82:18[c]	87
14		**10b**	C	10/80	**14m + 15m** 91:9[c]	70
15		**11a**	A	10/80	**14n**	91
16		**11b**	C	10/80	**14o**	71
17		**12a**	A	10/80	**14p**	73
18		**12b**	B	24/80		0
19		**13**	A	10/80	**14q**[e]	80
20	**6**	**10a**	C	96/80	**14r**	50

[a] A: 1 mol % $Pd(PPh_3)_4$ + 2 mol % PPh_3. B: 5 mol % $Pd(PPh_3)_4$ + 5 mol % dppe. C: 5 mol % $Pd(PPh_3)_4$. [b] Isolated yield. [c] Determined by ^1H NMR and GLC. [d] *E*/*Z* = 78/22. [e] *E*/*Z* = 56/44.

Table III. Palladium-Catalyzed Allylic Alkylation and Amination of Acyclic Primary Nitro Compounds[a]

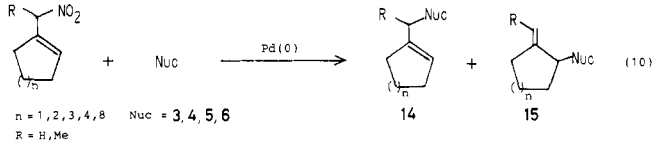
entry	nucleophile	nitro compound (R^1, R^2)	time, h/temp, °C	product (*E*/*Z*)[b]	yield, %[c]
1	**3**	**17** (Et, Me) (*E*/*Z* = 82/18)	19/70	**21a + 22a** (63/37) 29:71[b]	66
2	**4**	**17**	24/25	**22b** (76/24)	63
3		**18** (*n*-Pr, Et) (*E*/*Z* = 65/35)	24/25	**22c** (–)[d]	45
4		**19** (Me, $(CH_2)_2CO_2Me$) (*E*/*Z* = 71/29)	24/25	**21d + 22d** (*E*) 27:73[b]	71
5		**20** (Ph, Me) (*E*/*Z* = 47/53)	24/25	**22e** (74/26)	52
6	**5**	**17**	10/80	**21f + 22f** (63/37) 30:70[b]	97
7	**6**	**17**	14/80	**21g + 22g** (82/18) 35:65[b]	56

[a] Reactions were carried out with 5 mol % of $Pd(PPh_3)_4$ and dppe. [b] Determined by ^1H NMR and GLC. [c] Isolated yield. [d] Undetermined.

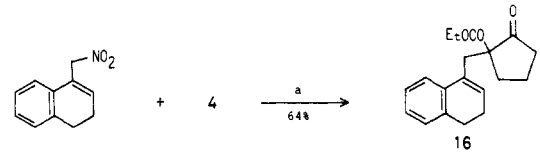
No reaction occurred in the absence of Pd(0) catalyst.

The above control of regiochemistry by modifying the steric bulk of the nucleophile was also observed in the case of amination of **1** and **2** (eq 9 and Table I). With piperidine (**5**), mixtures of regioisomers were obtained, whereas bulky di-*n*-propylamine (**6**) attacked exclusively at the less substituted terminus. In the amination, acetonitrile was a better solvent than THF in yield and easier to handle than DMF.

Cyclic allylic nitro compounds such as 1-(nitromethyl)cycloalkenes and 1-(1′-nitroethyl)cycloalkenes also underwent substitution by **3** and **5** in the presence of 1–5 mol % Pd(0) catalyst as shown in eq 10 and Table II.



DMF and acetonitrile were the suitable solvents for alkylation and amination, respectively. The reactions were highly regioselective, leading to substitution at the exocyclic carbon atom exclusively, except for the cyclohexenyl substrates **10a** and **10b**. In the case of **10a**, the use of bulky nucleophiles such as **4** and **6** resulted in the exclusive attack at the less substituted terminus (entries 10 and 20),[12] whereas **10b** was inert to **4** and **6**. Regioselective alkylation with 1-(nitromethyl)-3,4-dihydronaphthalene was also accomplished by using **4** to give **16** in 64% yield (eq 11).



(a) $Pd(PPh_3)_4$–dppe, DMF, 20 °C, 18 h

Primary acyclic nitro compounds also reacted with carbon nucleophiles (**3** and **4**) and with secondary amines

(11) The regioselectivity of nucleophilic attack on (π-allyl)palladium complexes depends upon the nature of the attacking nucleophile as well as the structure of the π-allyl complex. (a) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416–3426. (b) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3426–3435.

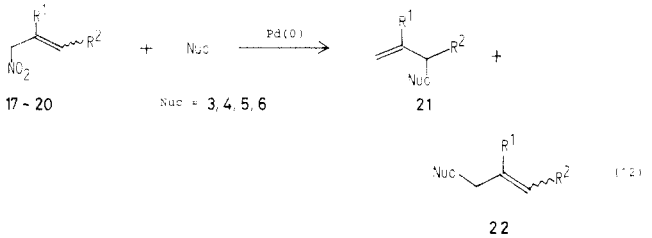
(12) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730–4743.

Table IV. Palladium-Catalyzed Denitro-amination of α-Nitro Olefins[a]

entry	R^1	R^2	R_2NH	product (E isomer)	yield, %[b]
1	Me	Me	**5**	**23a**	75
2	Et	Et	**5**	**23b**	70
3	Me	Et	**5**	**23c**	68
4	Et	Me	**5**	**24d (= 23c)**	72
5	$Me(CH_2)_4$	Me	**5**	**24e**	71
6	H	Et	**6**	**23f**	52
7	$(CH_2)_3$		**5**	**23g**	67[c]

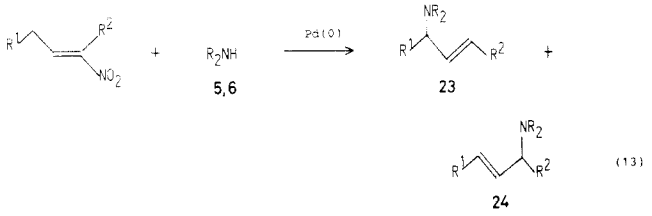
[a] Reactions were carried out with 5 mol % of $Pd(PPh_3)_4$ and dppe. [b] Isolated yield. [c] The initial yield of this material was considerably higher, but it decomposed during purification.

(**5** and **6**) to produce mixtures of regioisomers **21** and **22** (eq 12). The results are shown in Table III. With regard



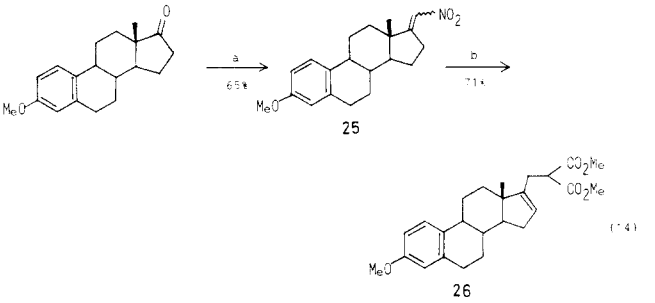
to alkylation with **17**, the regioselectivity was improved by using bulky nucleophile **4**. Interestingly, the regioselectivity of alkylation of **4** was influenced by the nature of substituent R^1 on the allylic unit: when R^1 was the phenyl group or the larger alkyl substituent than the methyl group, **22** was produced exclusively (entries 2–5). However, the use of bulky **6** did not affect regioselectivity in the amination (entries 6 and 7).

α,β-Disubstituted α-nitro olefins behave as secondary allylic nitro compounds by the action of a base and can be used directly as the substrate for allylic amination as shown in eq 13 and Table IV. Secondary amines act as



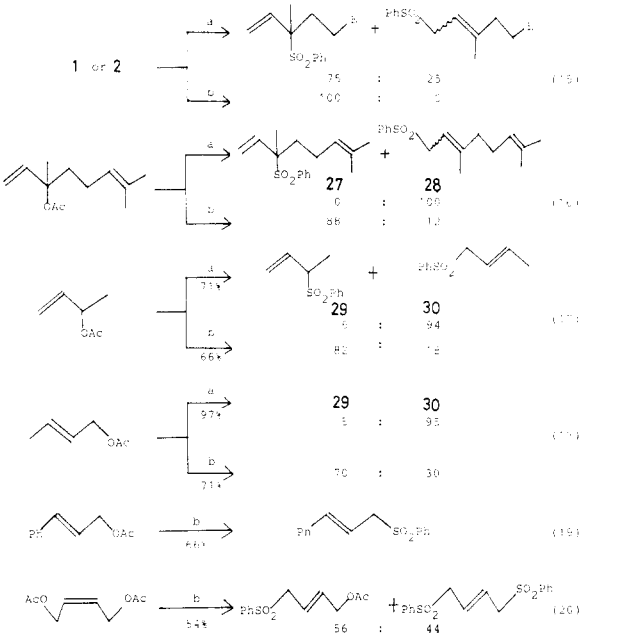
the base for isomerization as well as the nucleophile. DMF was the more suitable solvent than acetonitrile due to its acceleration effect on the isomerization of α-nitro olefins to the allylic forms. Reactions were highly regio- and stereoselective, attacking at the less hindered site and giving the E isomer exclusively.[13] Although attempted alkylation of **3** with these α-nitro olefins under the same conditions gave the corresponding Michael adducts without forming substitution products, α-nitro olefin **25**, prepared by N,N-dimethylethylenediamine-catalyzed condensation of estrone methyl ether with nitromethane,[14] was subjected to Pd(0)-catalyzed substitution by **3** to produce **26** in 71% yield (eq 14).

Sulfonylation. We have recently reported that the regiochemistry of Pd(0)-catalyzed allylic substitution of



(a) CH_3NO_2, $Me_2NCH_2CH_2NH_2$, PhH, reflux, 72 h; (b) **3**, $Pd(PPh_3)_4$–dppe, DMF, 70 °C, 4 h

tertiary allylic nitro compounds (**1** and **2**) and linalyl acetate by $PhSO_2^-$ is markedly affected by added $NaNO_2$: in the former case the exclusive formation of tertiary allylic sulfonesd was observed (eq 15), while in the latter case addition of $NaNO_2$ reversed the regioselectivity (eq 16).[2]



(a) $PhSO_2Na{\cdot}2H_2O$, $Pd(PPh_3)_4$, DMF, 70 °C, 3 h; (b) $PhSO_2Na{\cdot}2H_2O$, $Pd(PPh_3)_4$, $NaNO_2$, DMF, 20 °C, 15 h

This result indicates that the Pd(0) catalyst was deactivated by $NaNO_2$ to generate a new palladium species that is active enough to undergo the oxidative addition of allylic nitro compound and allylic acetate but is inert to allylic sulfone. Eventually, tertiary allylic sulfones are obtained as the product of kinetic control, without isomerization by the deactivated Pd catalyst to primary allylic sulfones, the product of thermodynamic control.[2,15]

In order to determine the optimum condition for obtaining the product of kinetic control by the regiocontrolled allylic substitution of a variety of allylic nitro compounds and allylic acetates by $PhSO_2^-$, the effect of solvents, other additives than $NaNO_2$, and various phosphorus ligands upon the regiochemistry were examined. Linalyl acetate was chosen as the substrate because the use of **1** or **2** may complicate the experimental results due to NO_2^- eliminated from **1** or **2** during the reaction.[2] Reaction of linalyl acetate with $PhSO_2Na{\cdot}2H_2O$ using 5 mol % $Pd(PPh_3)_4$ was carried out under various conditions. As shown in Table V, in the presence of $NaNO_2$, DMF or Me_2SO prevails over

(13) A similar regio- and stereoselectivity has been reported in the Pd-catalyzed allylic substitution of allylic acetates with morpholine. Keinan, E.; Sahai, M. *J. Chem. Soc., Chem. Commun.* **1984**, 648–650.

(14) Condensation of 17-oxo steroid with nitromethane in the presence of a catalytic amount of ethylenediamine has been reported to give the corresponding α-nitro olefin. Barton, D. H. R.; Motherwell, W. B.; Zand, S. Z. *J. Chem. Soc., Chem. Commun.* **1982**, 551–552. However, this procedure was not effective for the condensation of estrone methyl ether with nitromethane, giving a very small amount of the product **25**.

(15) (a) Inomata, K.; Yamamoto, T.; Kotake, H. *Chem. Lett.* **1981**, 1357–1360. (b) Julia, M.; Nel, M.; Righini, A.; Uguen, D. *J. Organomet. Chem.* **1982**, *235*, 113–120. Also see ref 20 and references therein.

Table V. Effect of Solvent and Additive on Regiochemistry[a]

entry	solvent	additive[b]	time, h/temp, °C	27:28[c]	yield, %[d]
1	THF–MeOH (v/v = 2/1)		15/20	0 100[e]	84
2	THF–MeOH	$NaNO_2$	15/20	47 53	72
3	DMF		3/70	0 100[f]	76
4	DMF	$NaNO_2$	3/70	80 20	72
5	DMF		15/20	58 42	90
6	DMF	$NaNO_2$	15/20	88 12	83
7	DMF	$NaNO_3$	15/20	72 28	72
8	DMF	KOCN	15/20	73 27	72
9	DMF	KSCN	15/20	63 37	58
10	DMF	LiCl	15/20	56 44	94
11	DMF	thiophene	15/20	78 22	93
12	Me_2SO		15/20	68 32	94
13	Me_2SO	$NaNO_2$	15/20	87 13	79

[a] Reactions were performed with 5 mol % of $Pd(PPh_3)_4$. [b] One equiv to linalyl acetate. [c] Determined by ^1H NMR. [d] Isolated yield. [e] E/Z = 74/26. [f] E/Z = 75/25.

Table VI. Effect of Phosphorus Ligand on Regiochemistry[a]

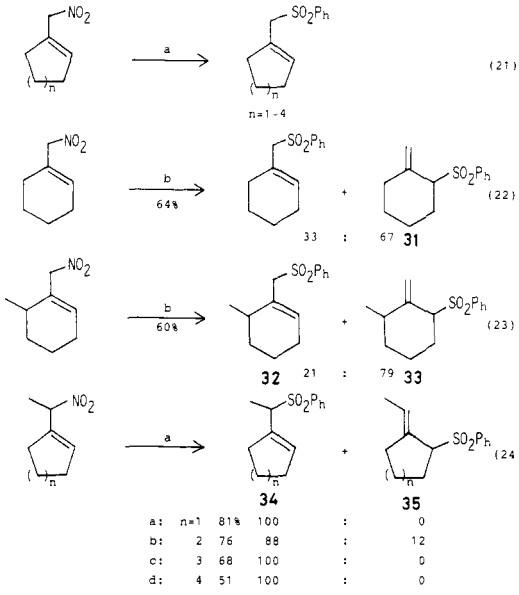
entry	ligand	mol %	27:28[b]	yield, %[c]
1	$(EtO)_3P$	20	67 33	61
2	PPh_3P	20	88 12	68
3	n-Bu_3P	20	77 23	51
4	dppe	10	68 32	68

[a] Reactions were performed with 5 mol % of $Pd(dba)_2$ and 1 equiv of $NaNO_2$. [b] Determined by ^1H NMR. [c] Isolated yield.

the mixed solvent of THF and methanol to lead to the prepondarant formation of tertiary allylic sulfone **27** (entries 2, 4, 6, and 13). Interestingly, even in the absence of $NaNO_2$, **27** was formed predominantly from the reaction carried out at 20 °C in DMF or Me_2SO, while the exclusive formation of **28** was observed in THF–methanol (entries 1, 5, and 12).[15] Among the additives examined in DMF, $NaNO_2$ showed the highest regioselectivity, giving a 88:12 mixture of **27** and **28**, from which **27** was easily isolated by column chromatography. To choose the most suitable phosphorus ligand for the palladium catalyst, linalyl acetate was allowed to react with $PhSO_2Na{\cdot}2H_2O$ in the presence of 5 mol % $Pd(dba)_2$ and 1 equiv of $NaNO_2$ using various ligands in DMF at 20 °C for 15 h. The results are shown in Table VI. PPh_3 showed the best preference for the formation of **27**, and other ligands possessing higher or lower basicity were inferior to PPh_3. Increasing the ratio of PPh_3 to $Pd(dba)_2$ to more than 4 caused a lowering of the regioselectivity, with the rise of the yield of the products. In contrast, the use of equimolar amounts of PPh_3 and $Pd(dba)_2$ resulted in the drop of the yield (36%) of the products without affecting the regioselectivity. The lowering of the yield was also observed when sulfonylation was performed using 5 mol % $Pd(PPh_3)_4$ and large excess (10 equiv) of $NaNO_2$ to linalyl acetate. Thus, when 5 mol % $Pd(PPh_3)_4$ and 1 equiv of $NaNO_2$ to linalyl acetate in DMF or Me_2SO were employed, the product **27** of kinetic control was preponderantly obtained.

The regiocontrolled allylic substitution of allylic acetates and other allylic nitro compounds by $PhSO_2^-$ using $Pd(PPh_3)_4$ and $NaNO_2$ or $Pd(PPh_3)_4$ alone was next studied. Both 3-acetoxy-1-butene and 1-acetoxy-2-butene were subjected to the regiocontrolled allylic substitution to afford the corresponding primary or secondary allylic sulfones selectively (eq 17 and 18). However, attempts to obtain secondary allylic sulfones from cinnamyl acetate and diacetoxy-*cis*-2-butene were unsuccessful, presumably owing to electronic effects of the substituents on the allylic unit (eq 19 and 20).[15]

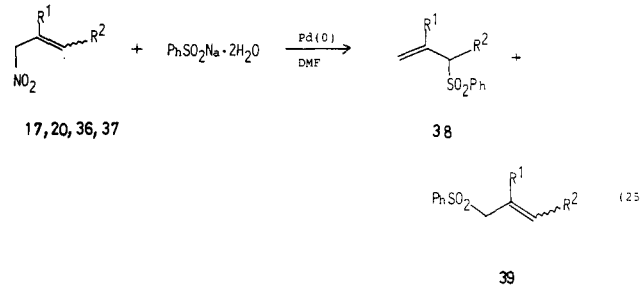
As already reported, 1-(nitromethyl)cycloalkenes react with $PhSO_2Na{\cdot}2H_2O$ in the presence of $Pd(PPh_3)_4$ to generate 1-(benzenesulfonylmethyl)cycloalkenes with high regioselectivity (eq 21).[2,7] Therefore, the synthesis of



(a) $PhSO_2Na{\cdot}2H_2O$, $Pd(PPh_3)_4$, DMF, 70 °C, 2 h; (b) $PhSO_2Na{\cdot}2H_2O$, $Pd(PPh_3)_4$, $NaNO_2$, DMF, 25 °C, 72 h

secondary allylic sulfones resulting from sulfonylation at the endocyclic carbon atom of the same substrates using $Pd(PPh_3)_4$–$NaNO_2$ system was attempted. From the cyclohexenyl substrate, secondary allylic sulfone **31** was obtained as the major product (eq 22). Methylation of the 6 position of the cyclohexene ring resulted in an increase of the proportion of sulfonylation at the endocyclic carbon atom (eq 23), while the exclusive formation of primary products was observed with five, seven, eight, and twelve member ring substrates. Examples of regioselective allylic sulfonylation with 1-(1-nitroethyl)cycloalkenes are shown in eq 24. Exclusive substitution at the exocyclic carbon atom occurred in five, seven, and eight member ring substrates regardless of addition of $NaNO_2$. Even in the case of cyclohexenyl substrate **10b**, addition of $NaNO_2$ did not affect the regioselectivity.

In the allylic sulfonylation with acyclic primary allylic nitro compounds, as shown in eq 25 and Table VII, the



product distribution was mainly influenced by the nature of substituent R^2 on the allylic unit: the order of the decreasing preference for the formation of secondary allylic sulfones **38** was Me > Et > *n*-pentyl when R^1 was an alkyl group, regardless of addition of $NaNO_2$. By adding $NaNO_2$, the proportion of the formation of **38** increased for **17**, **36**, and **37**, whereas no effect was observed for **20**, which gave **39d** as the major product.

α,β-Disubstituted α-nitro olefins served as excellent substrates for Pd-catalyzed allylic substitution by $PhSO_2^-$

Table VII. Palladium-Catalyzed Allylic Sulfonylation of Acyclic Primary Allylic Nitro Compounds

entry	nitro compound (R^1, R^2)	catalyst[a]	time, h/temp, °C	product (E/Z)[b]	yield, %[c]
1	**17** (Et, Me)	A	2/70	**38a** + **39a** (56/44) 52:48[b]	80
2		B	24/25	**38a** + **39a** (–)[d] 82:18[b]	71
3	**36** (Me, Et) (E/Z = 74/26)	A	2/70	**38b** + **39b** (80/20) 23:77[b]	85
4		B	48/25	**38b** + **39b** (75/25) 40:60[b]	58
5	**37** (Me, $(CH_2)_4Me$) (E/Z = 72/28)	A	3/70	**38c** + **39c** (72/28) 18:82[b]	64
6		B	24/25	**38c** + **39c** (78/22) 34:66[b]	79
7	**20** (Ph, Me)	A	2/70	**38d** + **39d** (20/80) 28:72[b]	63
8		B	24/25	**38d** + **39d** (14/86) 28:72[b]	52

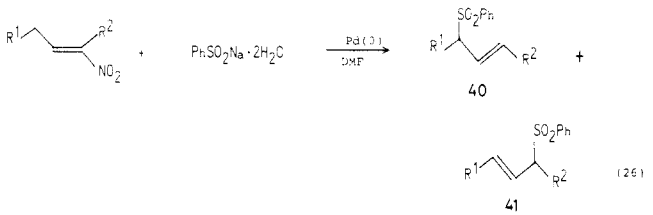
[a] A: 5 mol % $Pd(PPh_3)_4$. B: 5 mol % $Pd(PPh_3)_4$ + 1.0 equiv $NaNO_2$. [b] Determined by ^1H NMR and GLC. [c] Isolated yield. [d] Undetermined.

Table VIII. Palladium-Catalyzed Denitro-sulfonylation of α-Nitro Olefins[a]

entry	R^1	R^2	product (E isomer)	yield, %[b]
1	Me	Me	**40a**	81
2	Et	Et	**40b**	71
3	Me	Et	**40c** + **41c** 65:35[c]	80
4	Et	Me	**40c** + **41c** 62:38[c]	72
5	H	Et	**40d**	60
6			**40d** + **41d** 34:66[c]	38[d]
7	*e*		*f*	75
8	$(CH_2)_4$		**40e**	70

[a] Reactions were performed with 5 mol % of $Pd(PPh_3)_4$ and dppe and 1.0 equiv of Et_3N. [b] Isolated yield. [c] Determined by ^1H NMR and GLC. [d] One equiv of $NaNO_2$ was added and the reaction was carried out at 25 °C for 22 h. [e] $(CH_3)_2C{=}CHNO_2$. [f] $CH_2{=}C(CH_3)CH_2SO_2Ph$.

as shown in eq 26 and Table VIII. Pd catalyst was essential for this reaction. Addition of triethylamine and



dppe as a base to isomerize α-nitro olefins to the allylic form and as an additional ligand of Pd, respectively, resulted in the great improvement in yields of allylic sulfones with high stereoselectivity. Exposure of 3-nitro-2-pentene to the $Pd(PPh_3)_4$–$NaNO_2$ system in the presence of Et_3N gave the corresponding secondary allylic sulfone **41d** predominantly (entry 6).

Allylic nitro compounds and some α-nitro olefins have been proven to serve as reactive substrates for Pd-catalyzed allylic alkylation, amination, and sulfonylation reactions. Since these nitro substrates are now directly available from the condensation of ketones and aldehydes with nitroalkanes, the above chemistry offers a new synthetic method to take carbonyl compounds to functionalized allylic systems.

Experimental Section

General. Melting points were taken with a Meihoh Sharp melting pointer and are uncorrected. Infrared spectra were recorded on either a Beckman Model 4200 or a Shimadzu IR-27G spectrometer and are reported in cm^{-1}. ^1H NMR spectra were measured with either a JEOL FX-90Q (90 MHz), a Varian XL-300 (300 MHz), or a Nicolet NTCFT 1180 (360 MHz) instrument using Me_4Si as the internal standard and are reported in δ. ^{13}C NMR spectra were recorded on a JEOL FX-90Q (22.5 MHz) instrument. GLC analyses were performed on a Shimadzu GC-3BT chromatograph using a column packed with Silicone SE 30 (3 mm × 2 m). Mass spectra were taken on a Hitachi M-80A mass spectrometer at an ionization energy of 20 eV. Analytical TLC was performed on Merck precoated silica gel 60 F-254 plates. Preparative TLC was performed on 10 × 20 cm plates coated with Merck silica gel 60 PF-254. Column chromatography was performed on Merck silica gel 60 (less than 230 mesh) under moderate pressure (3 atm). Elemental analyses were performed by the Kyoto University Microanalytical Laboratories.

Materials. Solvents were distilled before use: DMF and benzene from calcium hydride, THF from benzophenone ketyl, and acetonitrile from phosphorus pentoxide. Dimethyl malonate, 2-(ethoxycarbonyl)cyclopentanone, piperidine, di-*n*-propylamine, nitromethane, *N,N*-dimethylethylenediamine, 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), sodium benzenesulfinate dihydrate, sodium nitrite, sodium nitrate, potassium cyanate, potassium thiocyanate, lithium chloride, and thiophene were commercial samples and were used without further purification. Triphenylphosphine, 1,2-bis(diphenylphosphino)ethane (dppe), triethylphosphite, and tributylphosphine were purified by recrystallization or distillation.

Tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] and bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] were prepared by published procedures.[16,17] Allylic acetates were prepared by acetylation of the corresponding commercially available allylic alcohols. α-Nitro olefins were prepared by published procedures.[18] Cyclic primary and secondary as well as acyclic primary allylic nitro compounds were prepared from ketones and nitroalkanes by the procedure shown in the previous paper.

Preparation of Methyl 4-Methyl-4-nitro-5-hexenoate (1). To a mixture of 2-nitro-2-butene (1.0 g, 10 mmol) and methyl acrylate (1.7 g, 20 mmol) in acetonitrile (30 mL) was added DBU (0.15 g, 1.0 mmol). The reaction mixture was stirred at room temperature for 15 h and ether (100 mL) was added. The ether solution was washed with aqueous 2 N HCl solution (30 mL) and water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification by distillation (115 °C/6.5 torr) gave 1.2 g (63%) of 1: IR (neat) 1737, 1535, 990, 938 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.17 (dd, J = 10.7, 17.5 Hz, 1 H), 5.38 (d, J = 10.7 Hz, 1 H), 5.34 (d, J = 17.5 Hz, 1 H), 3.66 (s, 3 H), 2.48–2.27 (m, 4 H), 1.67 (s, 3 H). Anal. ($C_8H_{13}NO_4$) C, H, N.

5-Methyl-5-nitro-6-hepten-2-one (2) was prepared with 3-buten-2-one (1.4 g, 20 mmol) by the same procedure.

(16) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(17) Takahashi, Y.; Ito, Ts.; Sakai, S.; Ishii, Y. *J. Chem. Soc. D* **1970**, 1065–1066.
(18) (a) Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*, 2138–2139. (b) Corey, E. J.; Estreicher, H. *J. Am. Chem. Soc.* **1978**, *100*, 6294–6295.

2: bp 83 °C/0.73 torr; IR (neat) 1718, 1540, 994, 940 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.12 (dd, J = 10.9, 17.4 Hz, 1 H), 5.34 (d, J = 10.9 Hz, 1 H), 5.30 (d, J = 17.4 Hz, 1 H), 2.50–2.22 (m, 4 H), 2.13 (s, 3 H), 1.65 (s, 3 H). Anal. ($C_8H_{13}NO_3$) C, H, N.

General Procedure for the Allylic Alkylation. The carbanions were prepared by adding **3** or **4** (3.0 mmol) to a slurry of pentane-washed sodium hydride (3.0 mmol) in DMF (8 mL) and stirring until homogeneous.

To a mixture of the allylic nitro compound (2.0 mmol), Pd(PPh_3)$_4$ (0.02–0.10 mmol), and PPh_3 (2 equiv to Pd) or dppe (1 equiv to Pd) if necessary in DMF (2 mL) under argon was added a DMF solution of the carbanion at room temperature. The combined mixture was stirred at 25 or 70 °C for the stated period of time (see tables). The reaction mixture was partitioned between ether and water, and the aqueous phase was extracted with ether (3 × 30 mL). The ether extracts were washed with brine (3 × 30 mL) and water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude products obtained in this manner could be purified by Kugelrohr disillation or column chromatography (9:1 hexane–ethyl acetate).

Dimethyl 2-(Methoxycarbonyl)-3-methyl-3-ethenyl-1,6-hexanedioate (7a) and dimethyl (*E*)-2-(methoxycarbonyl)-5-methyl-4-octene-1,8-dioate (8a): bp 125–130 °C/0.73 torr. The ratio of **7a** to **8a** was 13:87 as determined by GLC analysis. Separation of the two regioisomers was accomplished by preparative GLC to give pure **7a** and **8a**.

7a: IR (neat) 1750, 1732, 917, 990 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.88 (dd, J = 10.5, 17.6 Hz, 1 H), 5.13 (d, J = 10.5 Hz, 1 H), 5.03 (d, J = 17.6 Hz, 1 H), 3.67 (s, 3 H), 3.72 (s, 6 H), 3.42 (s, 1 H), 2.27–2.19 (m, 2 H), 1.94–1.87 (m, 2 H), 1.23 (s, 3 H). Anal. ($C_{13}H_{20}O_6$) C, H.

8a: IR (neat) 1750, 1732 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.09 (t, J = 7.6 Hz, 1 H), 3.72 (s, 6 H), 3.64 (s, 3 H), 3.35 (t, J = 7.9 Hz, 1 H), 2.59 (dd, J = 7.6, 7.9 Hz, 2 H), 2.41–2.33 (m, 2 H), 2.32–2.27 (m, 2 H), 1.62 (s, 3 H). Anal. ($C_{13}H_{20}O_6$) C, H.

Methyl (*E*)-4-methyl-6-(1-(ethoxycarbonyl)-2-oxocyclopent-1-yl)-4-hexenoate (8b): IR (neat) 1743, 1726 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.06 (t, J = 7.3 Hz, 1 H), 4.16 (q, J = 7.1 Hz, 2 H), 3.66 (s, 3 H), 2.62 (dd, J = 7.3, 14.3 Hz, 1 H), 2.50–2.15 (m, 2 H), 2.43–2.24 (m, 4 H), 2.18 (dd, J = 7.3, 14.3 Hz, 1 H), 2.15–1.74 (m, 4 H), 1.63 (s, 3 H), 1.25 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 214.9, 173.6, 171.1, 137.5, 119.5, 61.4, 60.4, 51.6, 38.2, 34.8, 32.8, 32.2, 31.9, 19.7, 16.3, 14.2. Anal. ($C_{16}H_{24}O_5$) C, H.

(*E*)-7-(1-(Ethoxycarbonyl)-2-oxocyclopent-1-yl)-5-methyl-5-hepten-2-one (8c): IR (neat) 1750, 1732 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.05 (t, J = 7.3 Hz, 1 H), 4.15 (q, J = 7.1 Hz, 2 H), 2.62 (dd, J = 7.3, 14.3 Hz, 1 H), 2.50–2.15 (m, 6 H), 2.19 (dd, J = 7.3, 14.3 Hz, 1 H), 2.14 (s, 3 H), 2.08–1.70 (m, 4 H), 1.63 (s, 3 H), 1.25 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 214.9, 208.2, 171.1, 137.6, 119.1, 61.3, 60.2, 42.0, 38.1, 33.6, 32.2, 31.7, 29.8, 19.6, 16.4, 14.1. Anal. ($C_{16}H_{24}O_4$) C, H.

Dimethyl 2-(1-cyclopent-1-ylmethyl)-1,3-propanedioate (14a): bp 95–100 °C/0.73 torr; IR (neat) 1752, 1734 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.39 (t, J = 1.7 Hz, 1 H), 3.73 (s, 6 H), 3.61 (t, J = 7.7 Hz, 1 H), 2.69 (d, J = 7.7 Hz, 2 H), 2.31–2.21 (br m, 4 H), 1.85 (m, 2 H). Anal. ($C_{11}H_{16}O_4$) C, H.

Methyl 2-(methoxycarbonyl)-3-(1-cyclopent-1-yl)butanoate (14b): bp 100 °C/0.10 torr. The spectral data of IR and ^1H NMR were identical with those of material prepared by an alternate procedure.[12]

Dimethyl 2-(1-cyclohexen-1-ylmethyl)-1,3-propanedioate (14c) and dimethyl 2-(2-methylenecyclohexyl)-1,3-propanedioate (15c): bp 120–125 °C/0.73 torr. The ratio of **14c** to **15c** was 79:21 as judged by ^1H NMR integration of the signals at δ 5.44 and 4.88, respectively. Separation of the regioisomers was accomplished by preparative GLC to give pure **14c** and **15c**.

14c: IR (neat) 1750, 1730 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.44 (t, J = 1.4 Hz, 1 H), 3.71 (s, 6 H), 3.56 (t, J = 8.1 Hz, 1 H), 2.53 (d, J = 8.1 Hz, 2 H), 1.98–1.84 (br m, 4 H), 1.63–1.44 (br m, 4 H). Anal. ($C_{12}H_{18}O_4$) C, H.

15c: 1752, 1730, 1648, 895 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 4.88 (s, 1 H), 4.78 (s, 1 H), 3.98 (s, 3 H), 3.97 (d, J = 10.5 Hz, 1 H), 3.33–3.25 (m, 1 H), 2.63–2.45 (br m, 2 H), 2.12–1.86 (br m, 6 H). Anal. ($C_{12}H_{18}O_4$) C, H.

Methyl 2-(methoxycarbonyl)-3-(1-cyclohexen-1-yl)butanoate (14d) and dimethyl 2-(2-ethylidenecyclohexyl)-1,3-propanedioate (15d): bp 110–115 °C/0.07 torr. The ratio of **14d** to **15d** was 65:35 as judged by ^1H NMR integration of the olefin proton signals of **14d** and **15d**. The spectral data of IR and ^1H NMR were identical with those of material prepared by an alternate procedure.[11]

Dimethyl 2-(1-cyclohepten-1-ylmethyl)-1,3-propanedioate (14e): bp 110 °C/0.73 torr; IR (neat) 1750, 1730 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.61 (t, J = 6.4 Hz, 1 H), 3.72 (s, 6 H), 3.54 (t, J = 7.8 Hz, 1 H), 2.57 (d, J = 7.8 Hz, 2 H), 2.11–2.02 (br m, 4 H), 1.71 (br m, 2 H), 1.51–1.38 (br m, 4 H). Anal. ($C_{13}H_{20}O_4$) C, H.

Methyl 2-(methoxycarbonyl)-3-(1-cyclohepten-1-yl)butanoate (14f): bp 115 °C/0.03 torr. The spectral data of IR and ^1H NMR were identical with those of material prepared by an alternate procedure.[12]

Dimethyl 2-(1-cycloocten-1-ylmethyl)-1,3-propanedioate (14g): bp 125 °C/0.03 torr; IR (neat) 1750 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.38 (t, J = 8.0 Hz, 1 H), 3.72 (s, 6 H), 3.61 (t, J = 7.7 Hz, 1 H), 2.60 (d, J = 7.7 Hz, 2 H), 2.32–1.92 (br m, 4 H), 1.74–1.23 (br m, 8 H). Anal. ($C_{14}H_{22}O_4$) C, H.

(*E*)- and (*Z*)-Dimethyl 2-(1-cyclododecen-1-ylmethyl)-1,3-propanedioate (14h): E/Z = 78/22; IR (neat) 1755, 1740 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ [5.40 (t, J = 7.7 Hz, 1 H) for **14hZ**], 5.16 (t, J = 7.7 Hz, 1 H), 3.71 (s, 6 H), 3.60 (t, J = 8.1 Hz, 1 H), [2.66 (d, J = 8.1 Hz, 2 H) for **14hZ**], 2.60 (d, J = 8.1 Hz, 2 H), 2.23–1.89 (br m, 4 H), 1.69–1.10 (br m, 16 H). Anal. ($C_{18}H_{30}O_4$) C, H.

2-(1-Cyclohexen-1-ylmethyl)-2-(ethoxycarbonyl)cyclopentanone (14i): IR (neat) 1756, 1728 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.43 (br, 1 H), 4.15 (q, J = 7.0 Hz, 2 H), 2.71 (d, J = 14.1 Hz, 1 H), 2.57–2.20 (m, 2 H), 2.23 (d, J = 14.1 Hz, 1 H), 2.10–1.89 (br m, 4 H), 1.87–1.64 (br m, 4 H), 1.62–1.40 (br m, 4 H), 1.25 (t, J = 7.0 Hz, 3 H). Anal. ($C_{15}H_{22}O_3$) C, H.

2-((3,4-Dihydronaphth-1-yl)methyl)-2-(ethoxycarbonyl)-cyclopentanone (16): IR (neat) 1756, 1728, 1451 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.36–7.03 (m, 4 H), 5.87 (t, J = 4.5 Hz, 1 H), 4.10 (q, J = 7.0 Hz, 2 H), 3.26 (d, J = 14.7 Hz, 1 H), 2.86 (d, J = 14.7 Hz, 1 H), 2.69 (t, J = 7.9 Hz, 2 H), 2.47–2.00 (m, 2 H), 2.23 (m, 2 H), 2.00–1.60 (m, 4 H). Anal. ($C_{19}H_{22}O_3$) C, H.

Methyl 4-ethyl-2-(methoxycarbonyl)-3-methyl-4-pentenoate (21a) and (*E*)- and (*Z*)-methyl 4-ethyl-2-(methoxycarbonyl)-4-hexenoate (22a): bp 150–155 °C/14 torr. The ratio of **21a** to **22a** was 29:71 as judged by ^1H NMR integration of the olefin proton signals at δ 4.79 and δ 5.31 and 5.22, respectively. Separation of the regioisomers was accomplished by preparative GLC to give pure **21a** and **22a**.

21a: IR (neat) 1756, 1742, 1648, 900 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 4.79 (br, 2 H), 3.51 (d, J = 7.5 Hz, 1 H), 2.94 (m, 1 H), 2.06 (q, J = 7.3 Hz, 2 H), 1.04 (t, J = 7.3 Hz, 3 H), 0.90 (d, J = 7.2 Hz, 3 H). Anal. ($C_{11}H_{18}O_4$) C, H.

22a: E/Z = 63/37; IR (neat) 1756, 1741, 1670, 822 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ [5.31 (q, J = 6.8 Hz, 1 H) for **22aZ**], 5.22 (q, J = 6.8 Hz, 1 H), 3.54 (t, J = 7.9 Hz, 1 H), [2.69 (d, J = 7.9 Hz, 2 H) for **22aZ**], 2.57 (d, J = 7.9 Hz, 2 H), 2.06 (q, J = 7.3 Hz, 2 H), 1.56 (d, J = 6.8 Hz, 3 H), 1.04 (t, J = 7.3 Hz, 3 H). Anal. ($C_{11}H_{18}O_4$) C, H.

(*E*)- and (*Z*)-2-(Ethoxycarbonyl)-2-(2-ethyl-2-buten-1-yl)cyclopentanone (22b): E/Z = 76/24; IR (neat) 1755, 1725 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ [5.40 (q, J = 6.5 Hz, 1 H) for **22bZ**], 5.20 (q, J = 6.5 Hz, 1 H), 4.16 (q, J = 7.0 Hz, 2 H), 2.77 (d, J = 14.2 Hz, 1 H), 2.47 (d, J = 14.2 Hz, 1 H), 2.51–2.14 (m, 2 H), 2.14–1.71 (br m, 4 H), 1.93 (q, J = 7.2 Hz, 2 H), 1.59 (d, J = 6.5 Hz, 3 H), 1.23 (t, J = 7.0 Hz, 3 H), 0.93 (t, J = 7.2 Hz, 3 H). Anal. ($C_{14}H_{22}O_3$) C, H.

2-(Ethoxycarbonyl)-2-(2-propyl-2-penten-1-yl)cyclopentanone (22c): IR (neat) 1757, 1725 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.15 (t, J = 7.1 Hz, 1 H), 4.14 (q, J = 7.0 Hz, 2 H), 2.76 (d, J = 14.1 Hz, 1 H), 2.63–2.13 (br m, 2 H), 2.24 (d, J = 14.1 Hz, 1 H), 2.13–1.71 (br m, 4 H), 1.91 (t, J = 7.2 Hz, 2 H), 1.71–1.14 (m, 4 H), 1.25 (t, J = 7.0 Hz, 3 H), 0.92 (2 t, J = 7.2 Hz, 6 H). Anal. ($C_{16}H_{26}O_3$) C, H.

Methyl 5-methyl-4-(1-(ethoxycarbonyl)-2-oxocyclopent-1-yl)-5-hexenoate (21d) and methyl (*E*)-5-methyl-6-(1-(ethoxycarbonyl)-2-oxocyclopent-1-yl)-4-hexenoate (22d). The

ratio of **21d** to **22d** was 27:73 as judged by ^{1}H NMR integration of the olefin proton signals at δ 4.87 and 5.15, respectively. For the mixture: IR (neat) 1755, 1737, 1725, 1643, 860 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.15 (t, J = 6.4 Hz, 1 H), [4.87 (s, 1 H), 4.78 (s, 1 H) for **21d**], 4.15 (q, J = 7.0 Hz, 2 H), 3.66 (s, 3 H), 2.77 (d, J = 14.3 Hz, 1 H), 2.40–2.24 (br m, 2 H), 2.35–2.30 (m, 4 H), 2.29 (d, J = 14.3 Hz, 1 H), 2.05–1.81 (m, 4 H), [1.63 (s, 3 H) for **21d**], 1.54 (s, 3 H). Anal. ($C_{16}H_{24}O_5$) C, H.

(*E*)- and (*Z*)-2-(Ethoxycarbonyl)-2-(2-phenyl-2-buten-1-yl)cyclopentanone (22e): E/Z = 74/26; IR (neat) 1756, 1726, 1445 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 5 H), 5.74 (q, J = 7.0 Hz, 1 H), [5.62 (q, J = 6.8 Hz, 1 H) for **22eZ**], 3.94 (dq, J = 10.7, 7.3 Hz, 1 H), 3.83 (dq, J = 10.7, 7.3 Hz, 1 H), 3.33 (d, J = 14.2 Hz, 1 H), [3.23 (d, J = 14.2 Hz, 1 H) for **22eZ**], 2.94 (d, J = 14.2 Hz, 1 H), [2.59 (d, J = 14.2 Hz, 1 H) for **22eZ**], 2.32–2.18 (m, 2 H), 1.89–1.70 (m, 4 H), 1.80 (d, J = 7.0 Hz, 3 H), 1.16 (t, J = 7.3 Hz, 3 H). Anal. ($C_{18}H_{22}O_3$) C, H.

Preparation of 3-Methoxy-17-(nitromethylene)-1,3,5(10)-estratriene (25). In a round-bottomed flask fitted with a Dean and Stark trap were placed estrone methyl ether (3.00 g, 10 mmol), nitromethane (18.3 g, 0.3 mol), *N*,*N*-dimethylethylenediamine (0.882 g, 10 mmol), and benzene (50 mL), and the mixture was refluxed for 72 h. The solvent and nitromethane were removed in vacuo and the resulting solid was washed with ether (50 mL). Purification by column chromatography (4:1 hexane–ethyl acetate) gave 2.23 g (65%) of a white solid, **25**: mp 195–196 °C dec; IR (Nujol) 1611, 1556, 1499 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, J = 8.8 Hz, 1 H), 6.92 (t, J = 2.5 Hz, 1 H), 6.73 (dd, J = 8.8, 2.6 Hz, 1 H), 6.64 (d, J = 2.6 Hz, 1 H), 3.79 (s, 3 H), 3.08 (dt, J = 2.5, 7.5 Hz, 2 H), 2.93–2.84 (m, 2 H), 2.48–2.38 (m, 1 H), 2.37–2.22 (m, 1 H), 2.02–1.92 (m, 3 H), 1.67–1.32 (m, 5 H), 0.97 (s, 3 H). Anal. ($C_{20}H_{25}NO_3$) C, H, N.

Alkylation of 25 with Dimethyl Malonate. A solution of dimethyl sodiomalonate (1.0 mmol) in DMF (3 mL) was added to a mixture of **25** (172 mg, 0.5 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), and dppe (10 mg, 0.025 mmol) in DMF (1 mL). The reaction mixture was heated at 70 °C for 4 h and worked up as in general procedure. Purification by column chromatography (9:1 hexane–ethyl acetate) gave 146 mg (71%) of 21,21-bis(methoxycarbonyl)-3-methoxy-19-norpregna-1,3,5(10),16-tetraene (**26**) as a colorless oil: IR (neat) 1758, 1740, 1610, 1500 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, J = 8.8 Hz, 1 H), 6.71 (dd, J = 8.8, 2.6 Hz, 1 H), 6.63 (d, J = 2.6 Hz, 1 H), 5.32 (br, 1 H), 3.78 (s, 3 H), 3.75 (s, 3 H), 3.74 (s, 3 H), 3.70 (t, J = 7.9 Hz, 1 H), 2.88 (m, 2 H), 2.64 (d, J = 7.9 Hz, 2 H), 2.40–2.31 (m, 1 H), 2.30–2.19 (m, 1 H), 2.19–2.07 (m, 1 H), 1.99–1.82 (m, 3 H), 1.67–1.34 (m, 5 H), 0.78 (s, 3 H). Anal. ($C_{25}H_{32}O_5$) C, H.

General Procedure for Allylic Amination of Allylic Nitro Compounds. To a mixture of the allylic nitro compounds (2.0 mmol), $Pd(PPh_3)_4$ (0.02–0.10 mmol), and PPh_3 (2 equiv to Pd) or dppe (1 equiv to Pd) if necessary to acetonitrile (4 mL) under argon was added the amine (4.0 mmol). The combined mixture was heated at 80 °C for the stated period of time (see tables). The reaction mixture was diluted with ether (100 mL), washed with water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude products obtained in this manner could be purified by Kugelrohr distillation.

Methyl 4-methyl-4-piperidino-5-hexenoate (7d) and (*E*)- and (*Z*)-methyl 4-methyl-6-piperidino-4-hexenoate (8d): bp 95–100 °C/0.73 torr. The ratio of **7d** to **8d** was 47:53 as determined by ^{1}H NMR integration of the olefin proton signals at δ 5.76 and 5.29, respectively. Separation of the two regioisomers was accomplished by preparative GLC to give pure **7d** and **8d**.

7d: IR (neat) 1746, 990, 915 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.76 (dd, J = 10.8, 18.0 Hz, 1 H), 5.08 (d, J = 10.8 Hz, 1 H), 5.01 (d, J = 18.0 Hz, 1 H), 3.64 (s, 3 H), 2.42 (m, 4 H), 2.38–2.28 (m, 2 H), 1.89–1.70 (m, 2 H), 1.50 (m, 4 H), 1.39 (m, 2 H), 1.02 (s, 3 H). Anal. ($C_{13}H_{23}NO_2$) C, H. N.

8d: E/Z = 87/13; IR (neat) 1745 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.29 (t, J = 6.8 Hz, 1 H), 3.64 (s, 3 H), 2.92 (d, J = 6.8 Hz, 2 H), 2.43 (t, J = 7.7 Hz, 2 H), 2.35 (m, 4 H), 2.32 (t, J = 7.7 Hz, 2 H), [1.72 (s, 3 H) for **8dZ**], 1.63 (s, 3 H), 1.57 (m, 4 H), 1.46–1.36 (m, 2 H). Anal. ($C_{13}H_{23}NO_2$) C, H, N.

Methyl (*E*)- and (*Z*)-6-(dipropylamino)-4-methyl-4-hexenoate (8e): bp 100–105 °C/0.73 torr; E/Z = 88/12; IR (neat) 1735 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.27 (t, J = 6.3 Hz, 1 H), 3.65 (s, 3 H), 3.03 (d, J = 6.3 Hz, 2 H), 2.43 (t, J = 7.6 Hz, 2 H), 2.33 (t, J = 7.6 Hz, 2 H), 2.32 (t, J = 7.7 Hz, 4 H), [1.70 (s, 3 H), for **8eZ**], 1.63 (s, 3 H), 1.44 (tq, J = 7.7, 7.3 Hz, 4 H), 0.85 (t, J = 7.3 Hz, 6 H). Anal. ($C_{14}H_{27}NO_2$) C, H, N.

(*E*)- and (*Z*)-7-(Dipropylamino)-5-methyl-5-hepten-2-one (8f): bp 95–100 °C/0.12 torr; E/Z = 83/17; IR (neat) 1718 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.26 (t, J = 6.6 Hz, 1 H), 3.03 (d, J = 6.6 Hz, 2 H), 2.58 (t, J = 7.5 Hz, 2 H), 2.42 (t, J = 7.5 Hz, 2 H), 2.36 (t, J = 6.8 Hz, 4 H), 2.16 (s, 3 H), [1.70 (s, 3 H) for **8fZ**], 1.63 (s, 3 H), 1.46 (tq, J = 6.8, 7.5 Hz, 4 H), 0.87 (t, J = 7.5 Hz, 6 H). Anal. ($C_{14}H_{27}NO$) C, H, N.

1-(1-Cyclopenten-1-ylmethyl)piperidine (14j): bp 50–55 °C/0.73 torr; IR (neat) 1461 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.48 (t, J = 1.2 Hz, 1 H), 2.93 (s, 2 H), 2.46–2.17 (m, 8 H), 1.84 (m, 2 H), 1.55 (m, 4 H), 1.40 (m, 2 H); mass spectrum, m/e (relative intensity) 165.0 (p, 100), 164.0 (97), 150.0 (60), 137.0 (19), 136.1 (23), 124.1 (17), 122.0 (28).

1-(1-Cyclopenten-1-yl)-1-piperidinoethane (14k): bp 60–65 °C/0.73 torr; IR (neat) 1553, 1441 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.45 (br, 1 H), 3.05 (q, J = 6.4 Hz, 1 H), 2.57–2.09 (br m, 8 H), 1.85 (m, 2 H), 1.70–1.23 (br m, 6 H), 1.13 (d, J = 6.4 Hz, 3 H). Anal. ($C_{12}H_{21}N$) C, H, N.

1-(1-Cyclohexen-1-ylmethyl)piperidine (14l) and 1-(2-methylenecyclohexyl)piperidine (15l): bp 155–160 °C/13 torr. The ratio of **14l** to **15l** was 82:18 as judged by ^{1}H NMR integration of the olefin proton signals at δ 5.55 and 4.79, respectively. For the mixture: IR (neat) 1440, 997, 922 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.55 (br, 1 H), [4.79 (s, 1 H), 4.73 (s, 1 H) for **15l**], 2.76 (s, 2 H), 2.50–2.15 (br m, 4 H), 2.15–1.85 (br m, 4 H), 1.85–1.17 (br m, 10 H). Anal. ($C_{12}H_{21}N$) C, H, N.

1-(1-Cyclohexen-1-yl)-1-piperidinoethane (14m) and 1-(2-ethylidenecyclohexyl)piperidine (15m): bp 60 °C/0.10 torr. The ratio of **14m** to **15m** was 91:9 as judged by ^{1}H NMR integration of the olefin proton signals at δ 5.50 and 5.23, respectively. For the mixture: IR (neat) 1552, 1443 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.50 (br, 1 H), [5.23 (q, J = 6.4 Hz, 1 H) for **15m**], 2.52 (q, J = 6.6 Hz, 1 H), 2.41–2.17 (br m, 4 H), 2.07–1.83 (br m, 4 H), 1.80–1.23 (br m, 10 H), [1.52 (d, J = 6.4 Hz, 3 H) for **15m**], 1.10 (d, J = 6.6 Hz, 3 H). Anal. ($C_{13}H_{23}N$) C, H, N.

1-(1-Cyclohepten-1-ylmethyl)piperidine (14n): bp 105 °C/0.25 torr; IR (neat) 1443 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.66 (t, J = 6.8 Hz, 1 H), 2.76 (s, 2 H), 2.27–1.94 (br m, 8 H), 1.95–1.20 (br m, 12 H). Anal. ($C_{13}H_{23}N$) C, H, N.

1-(1-Cyclohepten-1-yl)-1-piperidinoethane (14o): bp 90 °C/0.02 torr; IR (neat) 1445 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.62 (t, J = 6.4 Hz, 1 H), 2.61 (q, J = 6.5 Hz, 1 H), 2.43–2.23 (br m, 4 H), 2.23–1.97 (br m, 4 H), 1.89–1.23 (br m, 12 H), 1.08 (d, J = 6.5 Hz, 3 H). Anal. ($C_{14}H_{25}N$) C, H, N.

1-(1-Cycloocten-1-ylmethyl)piperidine (14p): bp 110 °C/0.25 torr; IR (neat) 1442 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.48 (t, J = 8.1 Hz, 1 H), 2.81 (s, 2 H), 2.51–1.94 (br m, 8 H), 1.83–1.21 (br m, 14 H). Anal. ($C_{14}H_{25}N$) C, H, N.

(*E*)- and (*Z*)-1-(1-Cyclododecen-1-ylmethyl)-1-piperidine (14q): bp 130 °C/0.03 torr; E/Z = 56/44; IR (neat) 1556, 1467, 1443 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ [5.50 (t, J = 7.7 Hz, 1 H) for **14qZ**], 5.26 (t, J = 7.7 Hz, 1 H), [2.89 (s, 2 H) for **14qZ**], 2.78 (s, 2 H), 2.48–2.16 (br m, 4 H), 2.16–1.86 (br m, 4 H), 1.77–1.02 (br m, 22 H). Anal. ($C_{18}H_{33}N$) C, H, N.

(1-Cyclohexen-1-yl)dipropylamine (14r): bp 85 °C/0.15 torr; IR (neat) 1552, 1460 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.56 (br, 1 H), 2.86 (s, 2 H), 2.34 (t, J = 7.3 Hz, 4 H), 2.15–1.88 (br m, 4 H), 1.77–1.47 (br m, 4 H), 1.45 (tq, J = 7.3, 7.1 Hz, 4 H), 0.86 (t, J = 7.1 Hz, 6 H). Anal. ($C_{13}H_{25}N$) C, H, N.

3-Ethyl-2-piperidino-3-butene (21f) and (*E*)- and (*Z*)-2-ethyl-1-piperidino-2-butene (22f): bp 110–115 °C/15 torr. The ratio of **21f** to **22f** was 30:70 as judged by ^{1}H NMR integration of the olefin proton signals at δ 4.84 and δ 5.34 and 5.29, respectively. Separation of the two regioisomers was accomplished by preparative GLC to give pure **21f** and **22f**.

21f: IR (neat) 1650, 899 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.84 (s, 1 H), 4.76 (s, 1 H), 2.83 (q, J = 6.4 Hz, 1 H), 2.54–2.11 (br m, 4 H), 2.09 (q, J = 7.2 Hz, 2 H), 1.76–1.20 (br m, 6 H), 1.11 (d, J = 6.4 Hz, 3 H), 1.10 (t, J = 7.2 Hz, 3 H). Anal. ($C_{11}H_{21}N$) C, H, N.

22f: E/Z = 63/37; IR (neat) 785 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ [5.34 (q, J = 6.4 Hz, 1 H) for **22fZ**], 5.29 (q, J = 6.4 Hz,

1 H), [2.89 (s, 2 H) for **22fZ**], 2.79 (s, 2 H), 2.54–2.11 (br m, 4 H), 2.09 (q, J = 7.2 Hz, 2 H), 1.63 (d, J = 6.4 Hz, 3 H), 1.76–1.21 (br m, 6 H), 0.96 (t, J = 7.2 Hz, 3 H). Anal. ($C_{11}H_{21}N$) C, H, N.

2-(Dipropylamino)-3-ethyl-3-butene (21g) and (*E*)- and (*Z*)-1-(dipropylamino)-2-ethyl-2-butene (22g): bp 110–115 °C/15 torr. The ratio of **21g** to **22g** was 35:65 judged by ^{1}H NMR integration of the olefin proton signals at δ 4.83 and δ 4.69 and 4.29, respectively. For the mixture: IR (neat) 1668, 1644, 893, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ [4.83 (s, 2 H) for **21g**], [4.69 (q, J = 6.9 Hz, 1 H) for **22gZ**], 4.29 (q, J = 6.9 Hz, 1 H), [2.94 (s, 2 H) for **22gZ**], 2.86 (s, 2 H), [2.57 (q, J = 6.4 Hz, 1 H) for **21g**], 2.29 (t, J = 7.3 Hz, 4 H), 2.09 (q, J = 7.2 Hz, 2 H), 1.62 (d, J = 6.9 Hz, 3 H), 1.40 (tq, J = 7.3, 7.1 Hz, 4 H), [1.06 (d, J = 6.4 Hz, 3 H) for **21g**], 0.94 (t, J = 7.2 Hz, 3 H), 0.86 (t, J = 7.1 Hz, 6 H). Anal. ($C_{12}H_{25}N$) C, H, N.

General Procedure for Allylic Amination of α-Nitro Olefins. To a mixture of the α-nitro olefin (2.0 mmol), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol), and dppe (40 mg, 0.10 mmol) in DMF (4 mL) under argon was added the amine (4.0 mmol). The combined mixture was heated at 75 °C for 1 h. The reaction mixture was partitioned between ether and water, and the aqueous phase was extracted with ether (3 × 30 mL). The ether extracts were washed with brine (3 × 30 mL) and water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude products obtained in this manner could be purified by Kugelrohr distillation or column chromatography (4:1 hexane–ether).

(*E*)-2-Piperidino-3-pentene (23a): bp 125–130 °C/16 torr; IR (neat) 1664, 972 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (dq, J = 15.1, 4.6 Hz, 1 H), 5.38 (dd, J = 15.1, 6.5 Hz, 1 H), 2.85 (dq, J = 6.5, 6.4 Hz, 1 H), 2.64–2.23 (m, 4 H), 1.80–1.21 (m, 6 H), 1.67 (d, J = 4.6 Hz, 3 H), 1.13 (d, J = 6.4 Hz, 3 H). Anal. ($C_{10}H_{19}N$) C, H, N.

(*E*)-3-Piperidino-4-heptene (23b): bp 140–145 °C/15 torr; IR (neat) 976 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.54 (dt, J = 15.6, 5.7 Hz, 1 H), 5.22 (dd, J = 15.6, 7.9 Hz, 1 H), 2.69–2.25 (br m, 4 H), 2.44 (dt, J = 5.7, 4.3 Hz, 1 H), 2.05 (dq, J = 5.7, 7.3 Hz, 2 H), 1.74–1.19 (br m, 6 H), 1.57 (dt, J = 4.3, 7.1 Hz, 2 H), 1.00 (t, J = 7.3 Hz, 3 H), 0.82 (t, J = 7.1 Hz, 3 H). Anal. ($C_{12}H_{23}N$) C, H, N.

(*E*)-2-Piperidino-3-hexene (23c): bp 130–135 °C/13 torr; IR (neat) 973 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (dt, J = 15.6, 5.9 Hz, 1 H), 5.04 (dd, J = 15.6, 7.8 Hz, 1 H), 2.88 (dq, J = 7.8, 7.1 Hz, 1 H), 2.60–2.35 (br m, 4 H), 2.04 (dq, J = 5.9, 7.3 Hz, 2 H), 1.58 (m, 4 H), 1.42 (m, 2 H), 1.14 (d, J = 7.1 Hz, 3 H), 0.98 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 133.3, 130.9, 62.6, 50.7, 26.1, 25.4, 24.6, 17.8, 13.7. Anal. ($C_{11}H_{21}N$) C, H, N.

(*E*)-2-Piperidino-3-nonene (24e): IR (neat) 977 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.54 (dt, J = 14.8, 5.7 Hz, 1 H), 5.38 (dd, J = 14.8, 7.1 Hz, 1 H), 2.88 (dq, J = 7.1, 6.6 Hz, 1 H), 2.56–2.31 (br m, 4 H), 2.15–1.87 (m, 2 H), 1.77–1.39 (br m, 6 H), 1.38–1.12 (br m, 6 H), 1.14 (d, J = 6.6 Hz, 3 H), 0.88 (t, J = 5.7 Hz, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 132.1, 131.9, 62.8, 50.8, 32.4, 31.5, 29.1, 26.3, 24.8, 22.5, 18.0, 14.1. Anal. ($C_{14}H_{27}N$) C, H, N.

(*E*)-1-(Dipropylamino)-2-pentene (23f): IR (neat) 974 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.73 (dt, J = 15.6, 5.1 Hz, 1 H), 5.35 (dt, J = 15.6, 5.4 Hz, 1 H), 3.03 (d, J = 5.4 Hz, 2 H), 2.39 (t, J = 6.8 Hz, 4 H), 2.03 (dq, J = 5.1, 7.3 Hz, 2 H), 1.46 (tq, J = 6.8, 7.3 Hz, 4 H), 0.98 (t, J = 7.3 Hz, 3 H), 0.85 (t, J = 7.3 Hz, 3 H). Anal. ($C_{11}H_{23}N$) C, H, N.

1-Piperidino-2-cyclohexene (23g): bp 140–145 °C/16 torr; IR (neat) 731 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.03–5.74 (m, 1 H), 5.74–5.46 (m, 1 H), 3.43–2.97 (br m, 1 H), 2.67–2.32 (br m, 4 H), 2.10–1.83 (br m, 2 H), 1.83–1.10 (br m, 10 H); mass spectrum, m/e (relative intensity) 165.3 (p, 36), 150.3 (6), 137.2 (100), 122.2 (56), 111.2 (6), 98.3 (25), 84.2 (16).

General Procedure for Allylic Sulfonylation in the Presence of $Pd(PPh_3)_4$ Alone. A mixture of the allylic nitro compound or acetate (2.0 mmol), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol), and $PhSO_2Na{\cdot}2H_2O$ (800 mg, 4.0 mmol) in DMF (8 mL) was heated at 70 °C under argon for 2–3 h. The reaction mixture was partitioned between ether and water, and the aqueous phase was extracted with ether (3 × 30 mL). The ether extracts were washed with brine (3 × 30 mL) and water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude products obtained in this manner were purified by column chromatography (4:1 hexane–ethyl acetate). Separation of the regioisomers was accomplished by preparative TLC.

General Procedure for Allylic Sulfonylation in the Presence of $Pd(PPh_3)_4$ and $NaNO_2$ or Other Additive. A mixture of $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) and $NaNO_2$ (138 mg, 2.0 mmol) or other additive (2.0 mmol) in DMF (8 mL) was stirred under argon at room temperature for 30 min. To this mixture was added the allylic nitro compound or acetate (2.0 mmol) and $PhSO_2Na{\cdot}2H_2O$ (800 mg, 4.0 mmol), and the combined mixture was stirred at room temperature for the stated period of time (see Table V and eq 15–24). After addition of aqueous 0.04 M KCN solution (10 mL, 0.4 mmol), the mixture was partitioned between ether and water, and the aqueous phase was extracted with ether (3 × 30 mL). The extracts were washed with brine (3 × 30 mL) and water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude products were purified by column chromatography (4:1 hexane–ethyl acetate). Separation of the regioisomers was accomplished by preparative TLC.

The spectral data of IR and ^{1}H NMR of linalyl phenyl sulfone, geranyl and neryl phenyl sulfones, (*E*)-1,4-bis(phenylsulfonyl)-2-butene, and (*E*)-1-phenyl-3-(phenylsulfonyl)-1-propene were identical with those of authentic samples.[15,19]

(*E*)-1-Acetoxy-4-(phenylsulfonyl)-2-butene: IR (neat) 1740, 1587, 1446, 1307, 1235, 1145, 969 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.97–7.37 (m, 5 H), 5.72 (dt, J = 15.4, 5.1 Hz, 1 H), 5.60 (dt, J = 15.4, 4.1 Hz, 1 H), 4.49 (d, J = 4.1 Hz, 2 H), 3.77 (d, J = 5.1 Hz, 2 H), 2.04 (s, 3 H). Anal. ($C_{12}H_{14}O_4S$) C, H.

2-(Phenylsulfonyl)-3-butene (29) and (*E*)-1-(Phenylsulfonyl)-2-butene (30). The ratio of **29** to **30** was determined by ^{1}H NMR integration of the signals for the allylic methyl groups of **29** and **30**. The spectral data of IR and ^{1}H NMR were identical with those of material prepared by an alternate procedure.[20]

2-Methylene-1-(phenylsulfonyl)cyclohexane (31): mp 105–106 °C; IR (Nujol) 1632, 1304, 1141, 903 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.99–7.34 (m, 5 H), 4.87 (br s, 1 H), 4.37 (br s, 1 H), 3.64 (d, J = 5.1 Hz, 1 H), 2.74–2.60 (br m, 1 H), 2.60–2.43 (br m, 1 H), 2.36–2.20 (br m, 1 H), 2.20–2.06 (br m, 1 H), 2.06–1.43 (br m, 4 H). Anal. ($C_{13}H_{16}O_2S$) C, H.

6-Methyl-1-((phenylsulfonyl)methyl)-1-cyclohexene (32): IR (Nujol) 1313, 1155 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.96–7.34 (m, 5 H), 5.34 (t, J = 3.0 Hz, 1 H), 3.87 (d, J = 13.4 Hz, 1 H), 3.53 (d, J = 13.4 Hz, 1 H), 2.00–1.76 (br m, 3 H), 1.66–1.34 (br m, 4 H), 0.99 (d, J = 7.2 Hz, 3 H). Anal. $C_{14}H_{18}O_2S$) C, H.

3-Methyl-2-methylene-1-(phenylsulfonyl)cyclohexane (33): mp 96–96.5 °C; IR (Nujol) 1634, 1538, 1302, 1143, 902 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.99–7.34 (m, 5 H), 4.84 (br s, 1 H), 4.46 (br s, 1 H), 3.71 (d, J = 5.1 Hz, 1 H), 3.03–2.43 (br m, 2 H), 2.30–2.03 (br m, 1 H), 2.03–1.43 (br m, 4 H), 1.04 (d, J = 6.4 Hz, 3 H). Anal. ($C_{14}H_{18}O_2S$) C, H.

1-(Cyclopenten-1-yl)-1-(phenylsulfonyl)ethane (34a): IR (neat) 1585, 1311, 1145 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.97–7.37 (m, 5 H), 5.46 (br, 1 H), 3.89 (q, J = 7.0 Hz, 1 H), 2.57–2.09 (br m, 4 H), 1.83 (br m, 2 H), 1.47 (d, J = 7.0 Hz, 3 H). Anal. ($C_{13}H_{16}O_2S$) C, H.

1-(Cyclohexen-1-yl)-1-(phenylsulfonyl)ethane (34b) and 2-Ethylidene-1-(phenylsulfonyl)cyclohexane (35b). The ratio of **34b** to **35b** was 88:12 as determined by ^{1}H NMR integration of the olefin proton signals at δ 5.40 and 4.86, respectively. For the mixture: IR (neat) 1656, 1586, 1445, 1308, 1145 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.00–7.36 (m, 5 H), 5.40 (br, 1 H), [4.86 (q, J = 6.4 Hz, 1 H), 4.00 (d, J = 5.7 Hz, 1 H) for **35b**], 3.57 (q, J = 7.0 Hz, 1 H), 2.16–1.74 (br m, 4 H), 1.73–1.26 (br m, 4 H), 1.47 (d, J = 7.0 Hz, 3 H). Anal. ($C_{14}H_{18}O_2S$) C, H.

1-(Cyclohepten-1-yl)-1-(phenylsulfonyl)ethane (34c): IR (neat) 1585, 1446, 1303, 1141 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.97–7.34 (m, 5 H), 5.50 (t, J = 6.4 Hz, 1 H), 3.64 (q, J = 7.0 Hz, 1 H), 2.34–2.10 (br m, 2 H), 2.10–1.83 (br m, 2 H), 1.83–1.06 (br m, 6 H), 1.46 (d, J = 7.0 Hz, 3 H). Anal. ($C_{15}H_{20}O_2S$) C, H.

1-(Cycloocten-1-yl)-1-(phenylsulfonyl)ethane (34d): IR (neat) 1587, 1445, 1305, 1145 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$)

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δ 7.91–7.34 (m, 5 H), 5.49 (t, J = 8.2 Hz, 1 H), 3.67 (q, J = 7.0 Hz, 1 H), 2.43–1.86 (br m, 4 H), 1.60–1.09 (br m, 8 H), 1.48 (d, J = 7.0 Hz, 3 H). Anal. ($C_{16}H_{22}O_2S$) C, H.

3-Ethyl-2-(phenylsulfonyl)-3-butene (38a) and (*E*)- and (*Z*)-2-Ethyl-1-(phenylsulfonyl)-2-butene (39a). The ratio of **38a** to **39a** was determined by ^1H NMR integration of the olefin proton signals at δ 4.91 and δ 5.53 and 5.14, respectively.

38a: IR (neat) 1640, 1586, 1446, 1308, 1146, 907 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.94–7.34 (m, 5 H), 5.03 (s, 1 H), 4.91 (s, 1 H), 3.66 (q, J = 7.2 Hz, 1 H), 2.09 (q, J = 7.2 Hz, 2 H), 1.47 (d, J = 7.2 Hz, 3 H), 0.97 (t, J = 7.2 Hz, 3 H). Anal. ($C_{12}H_{16}O_2S$) C, H.

39a: IR (neat) 1586, 1446, 1319, 1132 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.94–7.36 (m, 5 H), [5.53 (q, J = 6.9 Hz, 1 H) for **39aZ**], 5.14 (q, J = 6.9 Hz, 1 H), [3.84 (s, 2 H) for **39aZ**], 3.71 (s, 2 H), 2.07 (q, J = 7.4 Hz, 2 H), 1.51 (d, J = 6.9 Hz, 3 H), 0.97 (t, J = 7.4 Hz, 3 H). Anal. ($C_{12}H_{16}O_2S$) C, H.

2-Methyl-3-(phenylsulfonyl)-1-pentene (38b) and (*E*)- and (*Z*)-2-Methyl-1-(phenylsulfonyl)-2-pentene (39b). The ratio of **38b** to **39b** was determined by ^1H NMR integration of the olefin proton signals at δ 4.71 and δ 5.70 and 5.40, respectively.

38b: IR (neat) 1644, 1588, 1326, 1136, 910 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 8.03–7.23 (m, 5 H), 5.03 (s, 1 H), 4.71 (s, 1 H), 3.43 (dd, J = 3.9, 10.8 Hz, 1 H), 2.29–1.86 (m, 2 H), 1.79 (s, 3 H), 0.91 (t, J = 7.2 Hz, 3 H). Anal. ($C_{12}H_{16}O_2S$) C, H.

39b: IR (neat) 1589, 1448, 1312, 1148 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.96–7.36 (m, 5 H), [5.70 (t, J = 6.4 Hz, 1 H) for **39bZ**], 5.40 (t, J = 6.4 Hz, 1 H), [3.83 (s, 2 H) for **39bZ**], 3.71 (s, 2 H), 1.93 (dq, J = 6.4, 7.2 Hz, 2 H), 1.77 (s, 3 H), 0.77 (t, J = 7.2 Hz, 3 H). Anal. ($C_{12}H_{16}O_2S$) C, H.

2-Methyl-3-(phenylsulfonyl)-1-octene (38c) and (*E*)- and (*Z*)-2-Methyl-1-(phenylsulfonyl)-2-octene (39c). The ratio of **38c** to **39c** was determined by ^1H NMR integration of the olefin proton signals at δ 4.67 and δ 5.40 and 5.00, respectively.

38c: IR (neat) 1645, 1589, 1448, 1310, 1146, 906 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.96–7.33 (m, 5 H), 5.00 (s, 1 H), 4.67 (s, 1 H), 3.51 (dd, J = 4.0, 11.0 Hz, 1 H), 2.29–1.69 (m, 2 H), 1.77 (s, 3 H), 1.43–1.00 (m, 6 H), 0.87 (t, J = 6.5 Hz, 3 H). Anal. ($C_{15}H_{22}O_2S$) C, H.

39c: IR (neat) 1588, 1448, 1313, 1136 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 8.00–7.39 (m, 5 H), [5.40 (t, J = 6.4 Hz, 1 H) for **39cZ**], 5.00 (t, J = 6.4 Hz, 1 H), [3.83 (s, 2 H) for **39cZ**], 3.73 (s, 2 H), 1.83 (m, 2 H), 1.76 (s, 3 H), 1.43–1.00 (m, 6 H), 0.86 (t, J = 6.4 Hz, 3 H). Anal. ($C_{15}H_{22}O_2S$) C, H.

3-Phenyl-2-(phenylsulfonyl)-3-butene (38d) and (*E*)- and (*Z*)-2-Phenyl-1-(phenylsulfonyl)-2-butene (39d). The ratio of **38d** to **39d** was determined by ^1H NMR integration of the olefin proton signals at δ 5.47 and δ 6.08 and 5.74, respectively.

38d: IR (neat) 1625, 1585, 1449, 1315, 1150, 912 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.91–7.29 (m, 5 H), 7.14 (s, 5 H), 5.54 (s, 1 H), 5.47 (s, 1 H), 4.24 (q, J = 7.2 Hz, 1 H), 1.63 (d, J = 7.2 Hz, 3 H). Anal. ($C_{16}H_{16}O_2S$) C, H.

39d: IR (neat) 1587, 1495, 1447, 1310, 1136 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.81–7.08 (m, 5 H), 7.17 (s, 5 H), 6.08 (q, J = 7.2 Hz, 1 H), [5.74 (q, J = 6.8 Hz, 1 H) for **39dE**], 4.36 (s, 2 H), [4.12 (s, 2 H) for **39dE**], 1.66 (d, J = 7.2 Hz, 3 H), [1.60 (d, J = 6.8 Hz, 3 H) for **39dE**]. Anal. ($C_{16}H_{16}O_2S$) C, H.

General Procedure for Allylic Sulfonylation of α-Nitro Olefins. A mixture of the α-nitro olefin (1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), dppe (20 mg, 0.05 mmol), triethylamine (101 mg, 1.0 mmol), and $PhSO_2Na{\cdot}2H_2O$ (400 mg, 2.0 mmol) in DMF (4 mL) was heated at 70 °C under argon for 2 h. The reaction mixture was partitioned between ether and water, and the aqueous phase was extracted with ether (3 × 30 mL). The ether extracts were washed with brine (3 × 30 mL) and water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude products obtained in this manner were purified by column chromatography (4:1 hexane–ethyl acetate). Separation of the regioisomers was accomplished by preparative TLC.

The spectral data of IR and ^1H NMR of 1-(phenylsulfonyl)-2-methyl-2-propene was identical with those of authentic sample.[20]

(*E*)-2-(Phenylsulfonyl)-3-pentene (40a): IR (neat) 1669, 1588, 1446, 1305, 1144, 965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88–7.80 (m, 2 H), 7.68–7.50 (m, 3 H), 5.51 (dq, J = 15.5, 5.7 Hz, 1 H), 5.40 (ddq, J = 15.5, 7.8, 1.3 Hz, 1 H), 3.64 (dq, J = 7.8, 6.9 Hz, 1 H), 1.65 (d, J = 5.7 Hz, 3 H), 1.42 (d, J = 6.9 Hz, 3 H). Anal. ($C_{11}H_{14}O_2S$) C, H.

(*E*)-3-(Phenylsulfonyl)-4-heptene (40b): IR (neat) 1664, 1587, 1446, 1307, 1145, 969 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2 H), 7.66–7.48 (m, 3 H), 5.42 (dt, J = 15.5, 6.4 Hz, 1 H), 5.18 (ddt, J = 15.5, 9.5, 1.5 Hz, 1 H), 3.35 (ddd, J = 3.3, 9.5, 11.0 Hz, 1 H), 2.18 (ddq, J = 3.3, 13.5, 7.5 Hz, 1 H), 1.98 (dtq, J = 6.4, 1.5, 7.5 Hz, 2 H), 1.64 (ddq, J = 11.0, 13.0, 7.5 Hz, 1 H), 0.94 (t, J = 7.5 Hz, 3 H), 0.86 (t, J = 7.5 Hz, 3 H). Anal. ($C_{13}H_{18}O_2S$) C, H.

2-(Phenylsulfonyl)-3-hexene (40c) and 3-(Phenylsulfonyl)-4-hexene (41c). The ratio of **40c** to **41c** was determined by ^1H NMR integration of the methine proton signals at δ 3.65 and 3.33, respectively. For the mixture: IR (neat) 1667, 1587, 1447, 1307, 1142, 967 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90–7.80 (m, 2 H), 7.68–7.50 (m, 3 H), 5.52–5.18 (m, 2 H), 3.65 (dq, J = 7.9, 7.0 Hz, 1 H), [3.33 (ddd, J = 3.3, 9.5, 11.0 Hz, 1 H), 2.10 (m, 1 H) for **41c**], 1.98 (dq, J = 8.5, 7.5 Hz, 2 H), [1.65 (dd, J = 1.8, 6.5 Hz, 3 H), 1.62 (m, 1 H) for **41c**], 1.42 (d, J = 7.0 Hz, 3 H), [0.93 (t J = 7.5 Hz, 3 H) for **41c**], 1.87 (t, J = 7.5 Hz, 3 H). Anal. ($C_{12}H_{16}O_2S$) C, H.

(*E*)-1-(Phenylsulfonyl)-2-pentene (40d) and 3-(Phenylsulfonyl)-1-pentene (41d). The ratio of **40d** to **41d** was determined by ^1H NMR integration of the signals for the CH_2SO_2 at δ 3.75 and the corresponding methine proton signal at δ 3.40, respectively.

40d: IR (neat) 1669, 1588, 1447, 1309, 1144, 965 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92–7.80 (m, 2 H), 7.68–7.50 (m, 3 H), 5.53 (dtt, J = 15.5, 0.8, 6.3 Hz, 1 H), 5.40 (dtt, J = 15.5, 1.4, 7.3 Hz, 1 H), 3.75 (dd, J = 8.0, 7.3 Hz, 2 H), 2.0 (ddq, J = 1.4, 6.3, 8.0 Hz, 2 H), 0.90 (t, J = 8.0 Hz, 3 H). Anal. ($C_{11}H_{14}O_2S$) C, H.

41d: IR (neat) 1642, 1588, 1448, 1310, 1147, 998, 913 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 8.00–7.34 (m, 5 H), 5.66 (ddd, J = 8.2, 9.0, 16.7 Hz, 1 H), 5.37 (d, J = 9.0 Hz, 1 H), 5.03 (d, J = 16.7 Hz, 1 H), 3.40 (ddd, J = 3.1, 8.2, 10.3 Hz, 1 H), 2.20 (m, 1 H), 1.65 (m, 1 H), 0.94 (t, J = 7.2 Hz, 3 H). Anal. ($C_{11}H_{14}O_2S$) C, H.

3-(Phenylsulfonyl)cyclohexene (40e): IR (neat) 1647, 1584, 1445, 1309, 1144, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91–7.84 (m, 2 H), 7.70–7.52 (m, 3 H), 6.10 (ddt, J = 10.3, 3.4, 2.3 Hz, 1 H), 5.79 (ddd, J = 10.3, 5.0, 2.5 Hz, 1 H), 3.77 (m, 1 H), 2.00 (m, 2 H), 1.95–1.70 (m, 3 H), 1.50 (m, 1 H). Anal. ($C_{12}H_{14}O_2S$) C, H.

Allylic Sulfonylation of Linalyl Acetate in the Presence of $Pd(dba)_2$, Phosphorus Ligand, and $NaNO_2$ (Table VI). A mixture of $Pd(dba)_2$ (58 mg, 1.0 mmol), the phosphorus ligand (0.1–0.2 mmol), and $NaNO_2$ (69 mg, 1.0 mmol) in DMF (4 mL) was stirred under argon at room temperature for 30 min. To this mixture was added linalyl acetate (196 mg, 1.0 mmol) and $PhSO_2Na{\cdot}2H_2O$ (400 mg, 2.0 mmol), and the combined mixture was stirred at room temperature for 15 h. Aqueous 0.04 M KCN solution (5 mL, 0.2 mmol) was added, the mixture was partitioned between ether and water, and the aqueous phase was extracted with ether (3 × 30 mL). The ether extracts were washed with brine (3 × 30 mL) and water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude products were purified by column chromatography (4:1 hexane–ethyl acetate).

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Registry No. **1**, 81769-17-7; **2**, 81769-16-6; **3**, 18424-76-5; **4**, 13697-91-1; **5**, 110-89-4; **6**, 142-84-7; **7a**, 81769-34-8; **7d**, 81769-30-4; (*E*)-**8a**, 64562-42-1; (*Z*)-**8a**, 81769-33-7; **8b**, 104507-59-7; **8c**, 104507-60-0; (*E*)-**8d**, 81769-28-0; (*Z*)-**8d**, 81769-29-1; (*E*)-**8e**, 81769-31-5; (*Z*)-**8e**, 81769-32-6; (*E*)-**8f**, 104507-61-1; (*Z*)-**8f**, 104507-62-2; **9a**, 2562-42-7; **9b**, 98810-07-2; **10a**, 5330-61-0; **10b**, 90087-64-2; **11a**, 52315-51-2; **11b**, 104489-06-7; **12a**, 104489-07-8; **12b**, 104489-09-0; (*E*)-**13**, 104489-10-3; (*Z*)-**13**, 104505-58-0; **14a**, 81769-18-8; **14b**, 74545-48-5; **14c**, 60045-25-2; **14d**, 67428-16-4; **14e**, 81769-24-6; **14f**, 74545-49-6; **14g**, 104507-63-3; (*E*)-**14h**, 104507-64-4; (*Z*)-**14h**, 104507-65-5; **14i**, 104507-66-6; **14j**, 81769-22-4; **14k**, 104507-67-7; **14l**, 104507-68-8; **14m**, 83822-65-5; **14n**, 104507-71-3; **14o**, 104507-72-4; **14p**, 104507-73-5; (*E*)-**14q**, 104507-74-6; (*Z*)-**14q**, 104507-75-7; **14r**, 104507-76-8; **15c**, 67428-13-1; **15d**, 67428-17-5;

15l, 104507-69-9; **15m**, 104507-70-2; **16**, 104507-95-1; (*E*)-**17**, 104488-74-6; (*Z*)-**17**, 104488-75-7; (*E*)-**18**, 104507-77-9; (*Z*)-**18**, 104507-78-0; (*E*)-**19**, 104488-90-6; (*Z*)-**19**, 104488-91-7; (*E*)-**20**, 104488-92-8; (*Z*)-**20**, 104488-93-9; **21a**, 104507-79-1; **21d**, 104507-85-9; **21f**, 104507-89-3; **21g**, 104507-92-8; (*E*)-**22a**, 104507-80-4; (*Z*)-**22a**, 104507-81-5; (*E*)-**22b**, 104507-82-6; (*Z*)-**22b**, 104507-83-7; **22c**, 104507-84-8; (*E*)-**22d**, 104507-86-0; (*E*)-**22e**, 104507-87-1; (*Z*)-**22e**, 104507-88-2; (*E*)-**22f**, 104507-90-6; (*Z*)-**22f**, 104507-91-7; (*E*)-**22g**, 104507-93-9; (*Z*)-**22g**, 104507-94-0; **23a**, 93548-39-1; **23b**, 93548-42-6; **23c**, 93548-43-7; **23f**, 93548-47-1; **23g**, 61862-37-1; **24e**, 104507-96-2; **25**, 89103-82-2; **25** (ketone), 1624-62-0; **26**, 104531-39-7; **27**, 91940-11-3; (*E*)-**28**, 56691-80-6; (*Z*)-**28**, 56881-52-8; **29**, 54897-36-8; **30**, 72863-24-2; **31**, 96921-49-2; **32**, 104507-97-3; **33**, 104507-98-4; **34a**, 98810-10-7; **34b**, 100229-88-7; **34c**, 104508-00-1; **34d**, 104508-01-2; **35b**, 104507-99-5; (*E*)-**36**, 104488-82-6; (*Z*)-**36**, 104488-83-7; (*E*)-**37**, 104488-86-0; (*Z*)-**37**, 104488-87-1; **38a**, 104508-02-3; **38b**, 84602-97-1; **38c**, 104508-06-7; **38d**, 104508-09-0; (*E*)-**39a**, 104508-03-4; (*Z*)-**39a**, 104531-55-7; (*E*)-**39b**, 104508-04-5; (*Z*)-39b, 104508-05-6; (*E*)-**39c**, 104508-07-8; (*Z*)-**39c**, 104508-08-9; (*E*)-**39d**, 104508-10-3; (*Z*)-**39d**, 104508-11-4; **40a**, 97663-40-6; **40b**, 97663-36-0; **40c**, 97663-37-1; **40d**, 82234-80-8; **40e**, 87413-32-9; **40f**, 49639-05-6; **41c**, 97663-38-2; **41d**, 104508-12-5; DPPE, 1663-45-2; $Pd(dba)_2$, 33677-55-3: $MeC(NO_2)$=CHMe, 4812-23-1; H_2C=$CHCO_2Me$, 96-33-3; H_2C=CHAc, 78-94-4; $Pd(PPh_3)_4$, 14221-01-3; PPh_3, 603-35-0; $MeNO_2$, 75-52-5; $Me_2N(CH_2)_2NH_2$, 108-00-9; $PhSO_2Na$, 873-55-2; $NaNO_2$, 7632-00-0; $PhSO_2CH_2CH$=$CHCH_2OAc$, 95177-57-4; $EtCH$=$C(Me)NO_2$, 6065-19-6; $EtC(NO_2)$=CHPr, 6187-24-2; $EtCH$=$C(Et)NO_2$, 4812-22-0; $MeC(NO_2)$=CHPr, 6065-17-4; $MeC(NO_2)$=$CH(CH_2)_3Pr$, 4812-25-3; $EtC(NO_2)$=CHMe, 6065-18-5; H_2C=$CHCH(Me)OAc$, 6737-11-7; (*E*)-$MeCH$=$CHCH_2OAc$, 7204-29-7; (*E*)-$PhCH$=$CHCH_2OAc$, 21040-45-9; (*E*)-$PhCH$=$CHCH_2SO_2Ph$, 16212-07-0; (*Z*)-$AcOCH_2CH$=$CHCH_2OAc$, 25260-60-0; (*E*)-$PhSO_2CH_2CH$=$CHCH_2SO_2Ph$, 62384-73-0; Me_2C=$CHNO_2$, 1606-30-0; 1-(nitromethyl)-3,4-dihydronaphthalene, 104489-04-5; 1-nitrocyclohexene, 2562-37-0; 1-nitrocycloheptene, 36291-53-9; linalyl acetate, 115-95-7; 1-((phenylsulfonyl)methyl)cyclohexene. 49639-03-4; 3-methyl-2-(nitromethyl)cyclohexene, 104489-00-1.

Quantitative Comparison of the Heteroatom Effects in the Methoxide Attachment to Pyrylium and Thiopyrylium Cations. Thermodynamics of the Isomerization of Pyrans and Thiopyrans

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The complete set of kinetic and equilibrium constants for the methoxide attachment to a series of 2,6-di-*tert*-butyl-4-arylpyrylium cations (aryl = XC_6H_4 with X = *p*-NO_2, *m*-Cl, *p*-Cl, H, *p*-Me, *p*-OMe, *p*-NMe_2) has been obtained in MeOH at 25 °C. These data complement those previously obtained by studying the methoxide attachment to the corresponding thiopyrylium cations. In both series the reaction involves the kinetically controlled formation of both the corresponding 2*H* and 4*H* adducts which equilibrate to form only the thermodynamically more stable 2*H* adduct. The observed kinetic patterns show that the rate-determining step is the combination of the nucleophile with the cation to give the adducts. Moreover, the experimental data indicate that the Leffler–Hammond postulate cannot give information on the position of the transition state along the reaction coordinate. Both kinetic and equilibrium constants for the formation of the 2*H* and 4*H* adducts are correlated with the σ^+ constants. The obtained ρ values show, for the pyrylium series, a greater sensitivity to the substituent effects with respect to the corresponding thiopyrylium series. From the equilibrium data we estimate that, in contrast with quantum mechanical calculations, the unsubstituted 2*H*-pyran is at least 4.6 kcal/mol more stable than the corresponding 4*H* isomer.

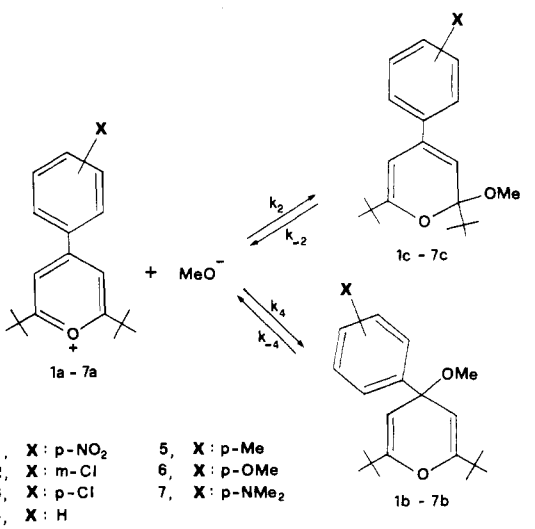
The chemistry of the ambident heteroaromatic cations, pyridinium, pyrylium, and thiopyrylium, presents a number of stimulating problems that attract the attention of the physical organic chemist. In particular, the reactivity of these cations with nucleophilic reagents can give valuable information about important topics, such as ring heteroatom effects, anion–cation combination reactions, and theoretical approaches to regioselectivity.

Here we wish to report a detailed kinetic and thermodynamic study of the methoxide attachment to 2,6-di-*tert*-butyl-4-arylpyrylium cations **1a–7a** in methanol at 25 °C to yield the corresponding 4*H*- (**1b–7b**) and 2*H*-pyrans (**1c–7c**).

These data complement those previously obtained by studying the methoxide attachment to the corresponding thiopyrylium cations **8–14** in methanol at 25 °C.[1]

Our aim is to assess in a quantitative and systematic way the role of the heteroatom on the electrophilic behavior of such ambident cations.

Scheme I



Results

^{1}H NMR Study. The ^{1}H NMR study of the reaction was performed at −30 °C and 30 °C, respectively.

The experiments carried out at −30 °C, with an excess of CD_3O^- in CD_3OD, lead to the immediate disappearance of the signals of the substrates and the appearance at

(1) Di Vona, M. L.; Doddi, G.; Ercolani, G.; Illuminati, G. *J. Am. Chem. Soc.* **1986**, *108*, 3409.

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