5.29 (10 H, s, Cp H), 3.29 (8 H, s, CH_2).

Anal. Calcd for $C_{26}H_{26}Ru_2P_2F_{12}$: C, 37.60; H, 3.16. Found: C, 37.33; H, 3.19.

Acknowledgment. We thank the National Science Foundation for support of this investigation (Grant No. CHE-7901763) and for financial aid in the purchase of a Nicolet 360 MHz spectrometer (Grant No. CHE-7922072). Also, we thank Richard Voegeli for his assistance in making the electrochemical measurements.

Registry No. **2**, 623-24-5; **3**, 10519-84-3; **4**, 85883-16-5; **5**, 65304-59-8; **6**, 87012-45-1; **7**, 87012-46-2; **10**, 87050-02-0; **11**, 87012-48-4; **12**, 1633-22-3; **13**, 87012-50-8; **14**, 87012-52-0; **16**, 4221-98-1; **17**, 52462-29-0; **18**, 71303-83-8; **21**, 77089-81-7; **22**, 77089-86-2; **23**, 71861-30-8; **24**, 87012-54-2; **25**, 80049-61-2; **26**, 80049-69-0; **27**, 87039-17-6; $RuCl_3$, 10049-08-8; bis(η^6-hexamethylbenzene)dichloro(di-μ-chloro)diruthenium(II), 67421-02-7; thiourea, 62-56-6; 1,4-bis(chloromethyl)durene, 3022-16-0.

A New Olefin Synthesis. Synchronous Elimination of Nitro and Ester Groups or Nitro and Keto Groups from β-Nitro Esters or β-Nitro Ketones[1]

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A new synthesis of α,β-unsaturated nitriles (**13**), esters (**14**), ketones (**15**), or sulfones (**16**) [$R^1R^2C{=}CR^3Y$, Y = CN (**13**), Y = COOEt (**14**), Y = C(=O)R (**15**), Y = SO_2R (**16**)] starting from α-bromonitroalkanes (**1**) or α-chloronitroalkanes (**2**) is presented. The reaction of **1** or **2** with ethyl α-alkylcyanoacetate (**3**), diethyl α-alkylmalonate (**4**), ethyl α-alkylacetoacetate (**5**), α-alkyl β-diketones (**6**), or ethyl α-alkyl-α-sulfonylacetate (**7**) followed by elimination of ethoxycarbonyl and nitro groups or acetyl and nitro groups gives **13**, **14**, **15**, and **16**. As the carbon–carbon bond-forming step proceeds via a free radical chain process, the reaction is less sensitive to steric hindrance than usual ionic reactions like aldol condensations, and highly substituted olefins are readily prepared.

In recent years we have studied the synthetic applications of the aliphatic nitro group as a leaving group for olefin synthesis.[3] We have found that the coupling products (**8**, **9**, **10**, **11**, and **12**) between α-halonitroalkanes (**1**, **2**) and α-cyano esters (**3**), geminal diesters (**4**), β-keto esters (**5**), β-diketones (**6**), or α-sulfonyl esters (**7**) can be converted into α,β-unsaturated nitriles (**13**), esters (**14**), ketones (**15**), or sulfones (**16**), respectively, by elimination of nitro and ester groups, or nitro and keto groups.[1] We now wish to report additional experimental data for this useful olefin synthesis which further extend its synthetic utility. The first coupling step proceeds via a one-electron-transfer chain process,[4-6] which has been studied extensively by Russell and co-workers.[4] The reaction of α-halonitroalkanes with stable carbanions was originally reported by van Tamelen and Van Zyl in 1949,[7] and since then various nucleophiles have been reported to react with **1** or **2**.[4,5]

The second elimination step can be performed by heating **8**, **9**, **10**, or **12** with sodium bromide or lithium chloride to cause deethoxycarbonylative elimination or by treating **11** or **12** with reducing agents to cause deacetylative elimination. In general, the nitro group fails to serve as a leaving group in substitution or elimination reactions by ionic processes, but the elimination of the nitro group takes place readily to give olefins if electron-withdrawing groups exist at a position β to the nitro function.[8] Although a number of methods already exist for olefin synthesis,[9] the present method gives a useful addition to them. It is especially useful for the preparation of highly substituted olefins, because the carbon–carbon bond-forming step proceeds very rapidly and is less sensitive to steric hindrance than the usual ionic processes such as aldol condensations or S_N2 reactions. In the present transfor-

Table I. Conversion of 8a into 13a by Heating with MX

solvent	MX	temp, °C	time, h	yield of 13a, %[a]
HMPA	NaBr	120	1.5	75
Me_2SO	NaBr	140	3	54
DMF	NaBr	140	3	40
HMPA	NaCl	120	3	10
HMPA	LiCl	120	3	74
Me_2SO	LiCl	140	3	70

[a] Isolated yields.

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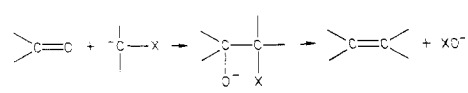
(9) A widely used method for olefin synthesis is carbonyl olefination represented by the following equation,



where X is PR_3, SiR_3, SR, SeR, etc.

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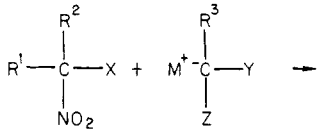
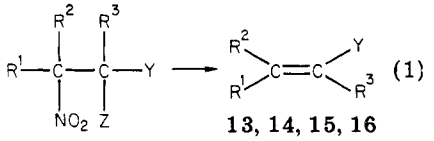
mations, the nitro group serves as an activating group for the carbon bond formation at the first step, and it serves as a leaving group at the next step.

Preparation of α,β-Unsaturated Nitriles (13). The reaction of 2-bromo-2-nitropropane (**1a**) with the sodium



1, 2 **3, 4, 5, 6, 7**



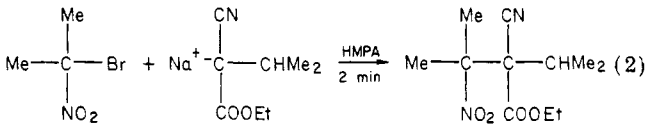
(1)

8, 9, 10, 11, 12 **13, 14, 15, 16**

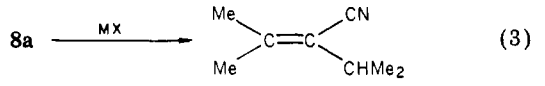
1, X = Br
2, X = Cl
3, 8, Y = CN; Z = COOEt
4, 9, Y = COOEt; Z = COOEt
5, 10, Y = C(O)Me; Z = COOEt
6, 11, Y = C(O)Me; Z = C(O)Me
7, 12, Y = SO_2Ar; Z = COOEt
13, Y = CN
14, Y = COOEt
15, Y = C(=O)Me
16, Y = SO_2Ar

salt of ethyl 2-cyanoisovalerate (**3a**) in hexamethylphosphoric triamide (HMPA) gave the coupling product (**8a**) in 73% yield. The reaction was very rapid; it was complete within 2 min at room temperature. This reaction was inhibited by the presence of 10 mol % of di-*tert*-butyl nitroxide, which suggests a free radical chain process for this reaction.

Heating **8a** with alkali metal salt (MX) in dipolar aprotic solvents resulted in clean elimination of the nitro and ethoxycarbonyl groups, giving the α,β-unsaturated nitrile **13a**.[10] The results are summarized in Table I. Sodium



1a **3a** **8a**, 73% (2)



(3)

13a

bromide or lithium chloride in HMPA or dimethyl sulfoxide (Me_2SO) were the most effective among the conditions tested for this transformation.

Compound **13a** can be prepared more conveniently by a one-pot procedure, because the same solvent can be used in both reactions 2 and 3 and the requisite sodium bromide to effect elimination is already formed in the coupling step. Thus, simply mixing **1a** and the sodium salt of **3a** in HMPA and heating the mixture at 120 °C for 1 h gave **13a** in 70% yield. This procedure can be extended to the general synthesis of trisubstituted α,β-unsaturated nitriles (**13**), where α-bromonitroalkanes (**1**) are obtained by bromination of nitroalkanes or bromination of oximes, and ethyl α-alkylcyanoacetates (**3**) were prepared by the alkylation of ethyl cyanoacetate. Results are summarized in Table II.

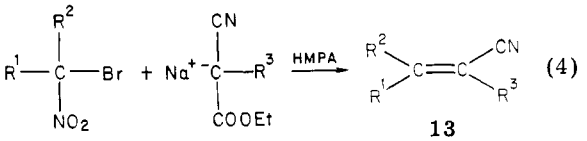
(10) Krapcho, A. P.; Weimaster, J. F.; Eldridge, J. M.; Jahngen Jr., E. G. E.; Lovey, A. J.; Stephens, W. P. *J. Org. Chem.* **1978**, *43*, 138.

Table II. Preparation of α,β-Unsaturated Nitriles (13) by a One-Pot Procedure

R^1	R^2	R^3	temp, °C	time, h	product, % yield[a]
Me	Me	i-C_3H_7	120	1.5	**13a**, 70
Me	Et	i-C_3H_7	140	1	**13b**, 62[b]
-$(CH_2)_5$-		i-C_3H_7	150	1	**13c**, 63
Me	Me	n-C_4H_9	150	1	**13d**, 72
-$(CH_2)_5$-		n-C_4H_9	140	1.5	**13e**, 65
Me	Me	n-C_6H_{17}	120	1	**13f**, 72
-$(CH_2)_5$-		n-C_6H_{17}	140	1	**13g**, 65
Me	Me	$PhCH_2$	120	1	**13h**, 75
Me	Et	$PhCH_2$	130	1	**13i**, 75[c]
-$(CH_2)_5$-		$PhCH_2$	140	1.5	**13j**, 69

[a] Isolated yields. [b] *E,Z* mixture, *E/Z* ratio = 1/1.3. [c] *E,Z* mixture, *E/Z* ratio = 1/1.2.

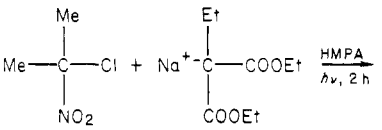
Preparation of α,β-Unsaturated Carbonyl Compounds (14, 15). α,β-Unsaturated esters (**14**) or ketones (**15**) are also expected to be prepared by the similar procedure of eq 4. However, the reaction of **1** with carbanions



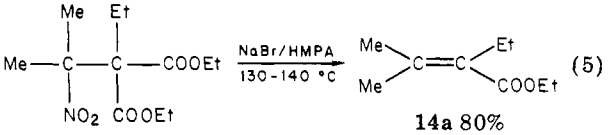
(4)

1 **3** **13**

derived from **4** or **5** does not give the coupling products (**9** and **10**) in good yields[4b,7] but results in extensive bromine atom transfer. Although α-nitro sulfones or α,α-dinitro compounds react with those anions to give **9** or **10** in good yields,[3c,4b,11] they are not as readily available as **1** or α-chloronitroalkanes (**2**).[12,13] On the other hand, 2-chloro-2-nitropropane (**2a**) was reported to react with the sodium or lithium salt of diethyl ethylmalonate (**4a**) to give **9a** in 68% yield.[4a,7] However, some modifications were necessary, because it took 36 h to complete the reaction by the original procedure. The reaction of **2a** with the sodium salt of **4a** was complete within 2 h at room temperature and yielded **9a** in 75% yield when HMPA or Me_2SO was used as a solvent and the reaction was irradiated by a 150-W tungsten lamp. Heating a stirred mixture of **9a** and sodium bromide in HMPA at 130–140 °C for 3 h resulted in clean formation of the α,β-unsaturated esters (**14a**).



2a **4a**



(5)

9a 75% **14a** 80%

Preparation of **14a** could be carried out more conveniently in one flask without isolation of **9a**. After irradiation of the reaction mixture, sodium bromide was added, and then the resulting mixture was heated at 130–140 °C to give **14a** in 63% overall yield.

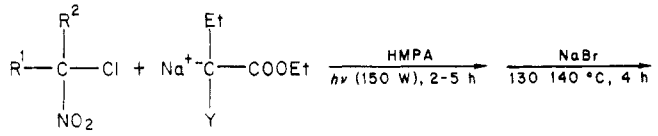
(11) Kornblum, N.; Boyd, S. D.; Ono, N. *J. Am. Chem. Soc.* **1974**, *96*, 2580.
(12) Kornblum, N.; Kestner, K. K.; Boyd, S. D.; Cattran, L. C. *J. Am. Chem. Soc.* **1973**, *95*, 3356.
(13) Kaplan, R. B.; Schecter, H. *J. Am. Chem. Soc.* **1961**, 83, 3535.

Table III. Preparation of α,β-Unsaturated Esters (14) or Ketones (15)

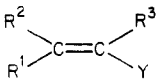
R^1	R^2	R^3	Y	product, % yield[a]
Me	Me	Et	COOEt	14a, 63[b]
$-(CH_2)_5-$		Et	COOEt	14b, 56[b]
Me	Me	n-C_4H_9	COOEt	14c, 69[c]
$-(CH_2)_5-$		n-C_4H_9	COOEt	14d, 42[c]
Me	Me	$PhCH_2$	COOEt	14e, 55[c]
Me	Me	Et	COMe	15a, 51[d]
Me	Me	n-C_4H_9	COMe	15b, 60[d]

[a] Isolated yields. [b] Irradiation for 2 h, heating for 3 h. [c] Irradiation for 4 h, heating for 4 h. [d] Irradiation for 5 h, heating for 4 h.

Trisubstituted α,β-unsaturated esters (14) or ketones (15) were thus prepared by the one-pot procedure (eq 6).



2 4, 5



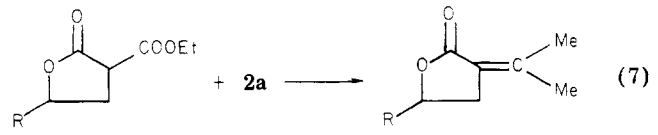
(6)

14, 15

4, 14, Y = COOEt
5, 15, Y = C(=O)Me

Addition of sodium bromide was necessary for smooth deethoxycarbonylation. The results are summarized in Table III.

The present procedure was further extended to the preparation of α-isopropylidene-γ-butyrolactones (**14f** and **14g**) and α-isopropylidenecyclopentanone (**15c**).



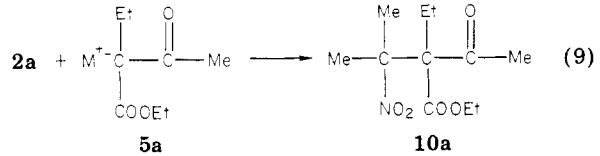
(7)

14f, R = H 50%
14g, R = Me 55%

(8)

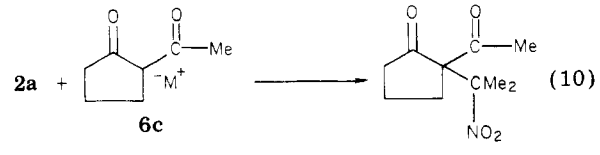
15c 54%

The reaction of **2** with the carbanions containing keto groups such as those derived from β-keto esters (**5**) or β-diketones (**6**) was significantly affected by light, solvent, and the cationic counterion of the carbanions. These effects were studied in the reaction of **2a** with the carbanions derived from ethyl 2-acetylbutylate (**5a**) or 2-acetylcyclopentanone (**6c**). The results are summarized in Table IV.



(9)

5a **10a**



(10)

6c **11c**

Table IV. Reaction of 2a with Anions Derived from 5a or 6c: Effects of Cation, Solvent, and Light

anion	cation (M^+)	solvent	light	time, h	product, % yield[a]
$5a^-$	K	Me_2SO	150 W	1	10a, 72
$5a^-$	Na	Me_2SO	150 W	1	10a, 42
$5a^-$	Li	Me_2SO	150 W	1	10a, 17
$5a^-$	K	DMF	150 W	1	10a, 55
$6c^-$	K	Me_2SO	150 W	1.5	11c, 95
$6c^-$	Na	Me_2SO	150 W	1.5	11c, 78
$6c^-$	Li	Me_2SO	150 W	1.5	11c, 63
$6c^-$	K	Me_2SO	dark	1.5	11c, 31
$6c^-$	K	THF	150 W	1.5	11c, 11

[a] GLC yields.

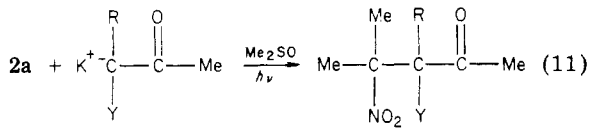
Table V. Preparation of β-Acetyl Nitro Compounds (10, 11) by the Reaction of Eq 14

R	Y	time, h	product, % yield[a]
Et	COOEt	1.5	10a, 69
n-C_4H_9	COOEt	2	10b, 65
$PhCH_2$	COOEt	2	10c, 77
n-C_4H_9	COMe	6	11b, 60
$CH_2CO(CH_2)_2CH_2$		2	11c, 75
Me	COMe	6	11d, 70

[a] Isolated yields.

The general trends of reactivity are Li < Na < K for the cation and THF < DMF < Me_2SO for the solvent.[14] Irradiation accelerates the reaction.

The β-acetyl nitro compounds (**10**, **11**) were prepared by the reaction of **2a** with the potassium salts of **5** or **6** in Me_2SO under irradiation by a 150-W tungsten lamp (eq 11; Table V).



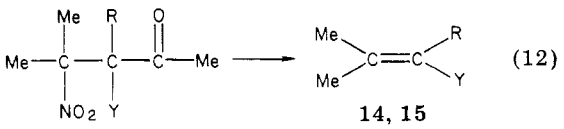
(11)

5, **6** **10**, **11**

5, 10, Y = COOEt
6, 11, Y = C(=O)Me

Elimination of the nitro and acetyl groups from **10** and **11** gave **14** and **15**, respectively. For example, treatment of **10a** with Li in ethylenediamine (EDA) gave **14a** in 64% yield. Generally, **14** could be prepared from **10** in about 60% yield by this procedure. However, the yield in the conversion of **11** to **15** by this procedure was very low. Milder reducing agents were desirable. The lithium salt of 2-nitropropane met this purpose.

Treatment of **11a** with the lithium salt of 2-nitropropane in HMPA under irradiation by a 150-W tungsten lamp produced **15c** in 78% yield. When the reaction was carried out in the dark, **15c** was obtained in 35% yield after the



(12)

10, **11** **14**, **15**

10, 14, R = COOEt
11, 15, R = C(O)Me

(14) Effect of ion pairing on the reactivity of anions toward the 2-nitro-2-propyl radical has been studied: Russell, G. A.; Ros, F.; Mudryk, B. *J. Am. Chem. Soc.* **1980**, *102*, 7601.

Table VI. Preparation of 14 or 15 from 10 or 11 with Reducing Agents

R	Y	reducing agent	solvent	time, h	product, % yield[a]
Et	COOEt	Li	EDA	4	14a, 64
n-C_4H_9	COOEt	Li	EDA	4	14c, 66
$PhCH_2$	COOEt	Li	EDA	5	14e, 61
Et	COOEt	Li-2NP[b]	HMPA[c]	12	14a, 35
n-C_4H_9	COMe	Li-2NP[b]	HMPA[c]	5	15b, 74
$CH_2CO(CH_2)_2CH_2$		Li-2NP[b]	HMPA[c]	5	15c, 78
Me	COMe	Li-2NP[b]	NMPA[c]	5	15d, 70

[a] Isolated yields. [b] $Li^+ {}^-CMe_2NO_2$. [c] Irradiation by a 150-W tungsten lamp.

Table VII. Preparation of α,β-Unsaturated Sulfones (16)

			preparation of 12		preparation of 16	
R^1	R^2	R^3	time, h	yield, %[a]	time, h	yield, %[a]
Me	Me	Me	5	12a, 80	2	16a, 87
Me	Me	Et	5	12b, 70	3	16b, 79
Me	Et	Me	10	12c, 65	3	16c, 71

[a] Isolated yield.

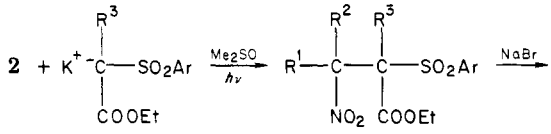
Table VIII. Stereochemistry of Alkoxylative Elimination from 8

R^2	R^3	A/B ratio of 8[a]	Z/E ratio of 13[b]
Et	$PhCH_2$	8i, 57/43	13i, 55/45
n-C_3H_7	$PhCH_2$	8k, 53/47	13k, 53/47
n-C_4H_9	$PhCH_2$	8l, 55/45	13l, 54/46
n-C_6H_{13}	$PhCH_2$	8m, 51/49	13m, 52/48
$PhCH_2$	Me_2CH	8n, 62/38	13n, 61/39

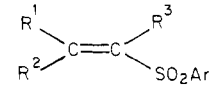
[a] The A/B ratio was determined by HPLC. [b] The Z/E ratio was determined by ^1H NMR.

same time. The conversion of **10** and **11** into **14** and **15** is summarized in Table VI.

Preparation of α,β-Unsaturated Sulfones (16). α,β-Unsaturated sulfones (**16**) were prepared by the reaction of **2** with the potassium salt of α-sulfonyl esters (**7**) and



7 **12**

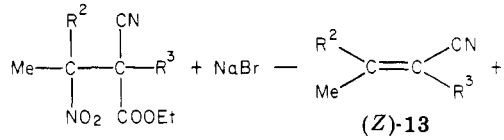


16 (13)

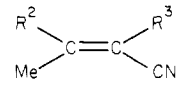
Ar = p-tolyl

the subsequent elimination of the nitro and ester groups. The reaction of **2** with anions of **7** proceeded slowly due to steric hindrance of the sulfonyl function. This reaction was accelerated by the use of potassium salts and by irradiation. Elimination of the ethoxycarbonyl and nitro groups was carried out by simply heating the coupling product (**12**) with sodium bromide at 130–140 °C in HMPA for 2–3 h. The results are summarized in Table VII.

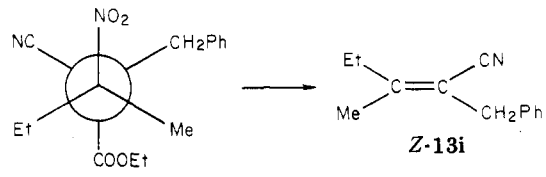
Stereochemistry of the Elimination. The alkoxylative elimination might be expected to proceed via either two routes: (i) a multistep mechanism involving carbanions as intermediates or (ii) a one-step concerted elimination. The former elimination would likely be nonstereospecific, and the latter stereospecific. The following experiments were done to study the stereochemistry of the elimination. When R^1 and R^2 are different, **8** consists of two diastereoisomers. The isomer of larger R_f value by TLC (silica gel plate/benzene) is called the **A** isomer, and the other the **B**-isomer. The ratio **A** isomer/**B** isomer could be determined by liquid chromatography (HPLC). Isomer **A** was formed in slight preference to isomer **B**. The results are summarized in Table VIII. Heating **8** with NaBr in HMPA resulted in the formation of a mixture of (*Z*)-**13** and (*E*)-**13**. The ratio (*Z*)-**13**/(*E*)-**13** was very close to the ratio **8-A**/**8-B**, which suggests that the elimination



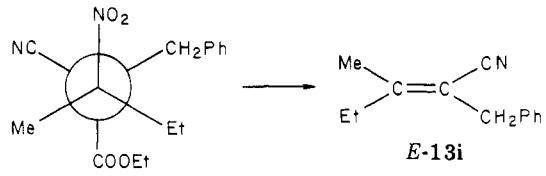
8 A, B (*Z*)-**13**



(*E*)-**13** (14)



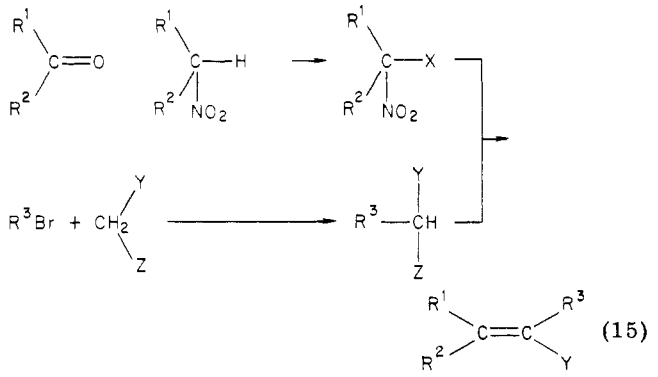
8i-A *Z*-**13i**



8i-B *E*-**13i**

is stereospecific. Stereospecificity was further confirmed by examining the products formed on elimination from the pure **A** and **B** isomers. Compound **8i** was separated into isomer **8i-A** and **8i-B** by column chromatography. Heating each isomer with NaBr in HMPA clearly gave (*Z*)-**13i** and (*E*)-**13i**, respectively. Because anti elimination is generally more favorable than syn elimination for the stereospecific process, **8i-A** is tentatively assigned as the *S,S* or *R,R* conformer and **8i-B** as a *R,S* conformer.

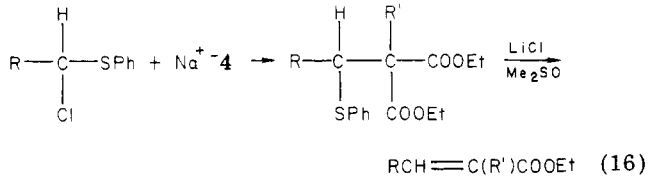
Scope and Limitation. Because **1** or **2** can be prepared from ketones or nitroparaffins and **3**–**7** can be prepared by alkylation of active methylene compounds by alkyl halides, various kinds of R^1, R^2, and R^3 can be introduced into olefins **13**–**16** (see eq 15). However, the present method has a severe limitation; it is not applicable when one of R^1–R^3 is hydrogen. If R^1 or R^2 is hydrogen, this hydrogen is readily abstracted by carbanions,[7] and if R^3 is hydrogen, nitrous acid is eliminated from the coupling product to give $R^1R^2C{=}CYZ$.[7,15] Thus, the present me-



13, 14, 15, 16

(15)

thod is limited to the synthesis of trisubstituted α,β-unsaturated olefins. However, mono- and disubstituted α,β-unsaturated carbonyl compounds or nitriles can be readily prepared by many known methods.[16] If α-chloro sulfides are used instead of **1** or **2**, the present procedure can be used for the preparation of mono- or disubstituted α,β-unsaturated esters[17] (eq 16). Mannich-type reactions



(16)

are especially effective for the synthesis of α-methylene carbonyl compounds.[18]

Experimental Section

NMR spectra were recorded on JEOL PS-100 spectrometers; chemical shifts are expressed in parts per million relative to Me_4Si. IR spectra were recorded on a Hitachi 215 spectrometer, and GLC analyses were performed on a Varian Aerograph 920 instrument equipped with a 2-m column packed with silicone DC-550. HPLC analyses were performed on a Hitachi 633A chromatograph with Hitachi gel 3010 and methanol as an eluent. GC–MS were measured on a Hitachi M-52 spectrometer (22 eV). Elemental analyses were performed by the Kyoto University Microanalytical Laboratories, and the results were within the accepted limits (±0.3%). All temperatures are uncorrected.

Materials. α-Halonitroalkanes (**1** and **2**) were prepared by halogenation of nitroalkanes[19] or oximes.[20] Compounds **3**, **4**, **5**, and **7** were prepared by alkylation of ethyl cyanoacetate, diethyl malonate, ethyl acetoacetate, or ethyl tosylacetate.[21] β-Dicarbonyl compounds (**6**) were prepared by acylation of ketones.[22] Reagent grade solvents were purified by standard techniques and kept over a drying agent.

Preparation of Ethyl 2-Cyano-2-(1′-nitro-1′-methylethyl)isovalerate (8a). A solution of ethyl 2-cyanoisovalerate (**3a**, 1.6 g, 10 mmol) in HMPA (5 mL) was added to a stirred suspension of NaH (50% dispersion, 11 mmol) in HMPA (20 mL) at room temperature under nitrogen, and then a solution of 2-bromo-2-nitropropane (**1a**, 1.7 g, 10 mmol) in HMPA (5 mL) was added. After 2 min, the mixture was poured into water (20 mL) and the product extracted with ether (3 × 50 mL). The organic layer was washed with water, dried with magnesium sulfate, and concentrated under reduced pressure. The residue was distilled to give **8a**: 1.9 g (73% yield); bp 126 °C (1 mmHg); IR (neat) 2245, 1730, 1540 cm^{-1}; NMR (CCl_4) δ 1.10 (3 H, t, J = 7.5 Hz), 1.50 (6 H, d, J = 7.5 Hz), 1.81 (3 H, s), 1.85 (3 H, s), 2.32 (1 H, q, J = 7.5 Hz), 4.18 (2 H, q, J = 7.5 Hz). Anal. Calcd for $C_{11}H_{18}N_2O_4$: C, 54.53; H, 7.49; N, 11.56. Found: C, 54.73; H, 7.30; N, 11.76.

The reaction of **3a** (1 mmol) with **1a** (1 mmol) was carried out in the presence of di-*tert*-butyl nitroxide (0.1 mmol) under the same conditions as above. The reaction product was analyzed by GLC using dimethyl malonate as an internal standard to reveal that **8a** was produced in only 1% yield.

Conversion of 8a into α,β-Unsaturated Nitriles (13a). A mixture of **8a** (2.4 g, 10 mmol) and sodium bromide (1.1 g, 11 mmol) in HMPA (20 mL) was stirred at 120 °C for 1.5 h and then poured into water (50 mL); the product was extracted with ether (3 × 100 mL). The organic layer was washed with water, dried with magnesium sulfate, concentrated under reduced pressure, and distilled to give **13a**: 0.92 g (75% yield); bp 62 °C (9 mmHg); IR (neat) 2220, 1620 cm^{-1}; NMR (CCl_4) δ 1.05 (6 H, d, J = 7.2 Hz), 1.81 (3 H, s), 2.01 (3 H, s), 2.63 (1 H, q, J = 7.2 Hz); MS (relative intensity) 123 (M^+, 44), 108 (100), 82 (44), 69 (56). Anal. Calcd for $C_8H_{12}N$: C, 78.00; H, 10.64; N, 11.37. Found: C, 77.81; H, 10.43; N, 11.51.

When **8a** and sodium bromide in Me_2SO (20 mL) were heated at 140 °C for 3 h, **8a** and sodium bromide in DMF (20 mL) at 140 °C for 3 h, **8a** and sodium chloride in HMPA (20 mL), **8a** and lithium chloride in HMPA (20 mL) at 120 °C for 3 h, or **8a** and lithium chloride in Me_2SO (20 mL) at 140 °C for 3 h, **13a** was isolated in 54%, 40%, 10%, 74%, or 70% yield, respectively.

One-Pot Synthesis of 13. Typical Procedure. A solution of **3a** (1.6 g, 10 mmol) in HMPA (10 mL) was added to a stirred suspension of NaH (11 mmol) in HMPA (20 mL) at room temperature under nitrogen and then a solution of **1a** (1.7 g, 10 mmol) in HMPA (5 mL) was added. The mixture was heated at 120 °C for 1.5 h and then poured into water; the product was extracted with ether. The organic layer was washed with water, dried with magnesium sulfate, concentrated under reduced pressure, and distilled to give **13a**, 0.86 g (70% yield). The following olefins were prepared by this procedure.

13b: bp 85 °C (12 mmHg); IR (neat) 2210, 1620 cm^{-1}; NMR (CCl_4) δ 0.88–1.29 (m, 9 H), 1.84 (1.7 H, s), 2.04 (1.3 H, s), 2.20 (0.9 H, q, J = 7.5 Hz), 2.38 (1.1 H, q, J = 7.5 Hz), 2.55–2.95 (m, 1 H); MS 137 (M^+).

13c: bp 125 °C (3 mmHg); IR (neat) 2210, 1615 cm^{-1}; NMR (CCl_4) δ 1.08 (6 H, d, J = 7.2 Hz), 1.62 (6 H, m), 2.27 (2 H, m), 2.44 (2 H, m), 2.75 (1 H, m); MS 163 (M^+).

13d: bp 95 °C (25 mmHg); IR (neat) 2210, 1630 cm^{-1}; NMR (CCl_4) δ 0.97 (3 H, t, J = 7.0 Hz), 1.2–1.6 (4 H, m), 1.85 (3 H, s), 2.08 (3 H, s), 2.19 (2 H, m); MS 137 (M^+).

13e: bp 144 °C (11 mmHg); IR (neat) 2200, 1620 cm^{-1}; NMR (CCl_4) δ 0.94 (3 H, t, J = 7.0 Hz), 1.1–1.95 (10 H, m), 2.06–2.40 (4 H, m), 2.40–2.60 (2 H, m); MS 177 (M^+).

13f: bp 97 °C (1 mmHg); IR (neat) 2220, 1630 cm^{-1}; NMR (CCl_4) δ 0.89 (3 H, t, J = 7.0 Hz), 1.10–1.60 (12 H, m), 1.84 (3 H, s), 2.06 (3 H, s), 2.17 (2 H, m); MS 193 (M^+).

13g: bp 105 °C (1 mmHg); IR (neat) 2200, 1619 cm^{-1}; NMR (CCl_4) δ 0.88 (3 H, m), 1.0–1.8 (20 H, m), 2.06–2.34 (4 H, m), 2.34–2.40 (2 H, m); MS 233 (M^+).

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13h: bp 96 °C (0.6 mmHg); IR (neat) 2200, 1630 cm^{-1}; NMR (CCl_4) δ 1.90 (3 H, s), 2.09 (3 H, s), 3.48 (2 H, s), 7.15 (5 H, m); MS 171 (M^+).

13i: IR (neat) 2210, 1625 cm^{-1}; NMR (CCl_4) δ 0.80–1.16 (3 H, m), 1.76 (1.6 H, s), 1.96 (1.4 H, s), 2.19 (0.9 H, q, J = 7.5 Hz), 2.35 (1.1 H, q, J = 7.5 Hz), 3.39 (2 H, s), 7.1 (5 H, m); MS 185 (M^+).

13j: IR (neat) 2205, 1620 cm^{-1}; NMR (CCl_4) δ 1.4–1.8 (6 H, m), 2.2–2.4 (2 H, m), 2.4–2.6 (2 H, m), 3.45 (2 H, s), 7.15 (5 H, m); MS 211 (M^+).

Preparation of α,β-Unsaturated Carbonyl Compounds (14, 15). Preparation of 2-(1-Nitro-1-methylethyl)-2-ethylmalonic Ester (9a). A solution of diethyl ethylmalonate (**4a**, 1.9 g, 10 mmol) in Me_2SO (5 mL) was added to a stirred suspension of NaH (11 mmol) in Me_2SO (20 mL) at room temperature under nitrogen, and then a solution of 2-chloro-2-nitropropane (**2a**, 1.3 g, 10 mmol) in Me_2SO (5 mL) was added. The reaction mixture was irradiated by a 150-W tungsten lamp for 2 h and then poured into water. The product was extracted with ether (3 × 50 mL), and the organic layer was washed with water, dried with magnesium sulfate, and concentrated under reduced pressure. The residue was distilled to give **9a**: 2.0 g (75% yield); bp 155 °C (10 mmHg) [lit.[7] 161–165 °C (14 mmHg)].

Conversion of 9a to 14a. A mixture of **9a** (2.75 g, 10 mmol and sodium bromide (3.1 g, 30 mmol) in HMPA (20 mL) was stirred at 130–140 °C for 4 h. After the usual workup, distillation gave **14a**: 1.27 g (80% yield); bp 95 °C (38 mmHg); IR (neat) 1700, 1620 cm^{-1}; NMR (CCl_4) δ 0.97 (3 H, t, J = 7.5 Hz), 1.27 (3 H, t, J = 7.5 Hz), 1.80 (3 H, se, 1.94 (3 H, s), 2.29 (2 H, q, J = 7.5 Hz), 4.14 (2 H, q, J = 7.5 Hz); MS 159 (M^+).

One-Pot Procedure To Prepare 14 and 15. Typical Procedure: Preparation of 14a. A solution of **4a** (1.9 g, 10 mmol) in HMPA (5 mL) was added to a stirred suspension of NaH (11 mmol) in HMPA (20 mL) at room temperature under nitrogen, and a solution of **1b** (1.3 g, 10 mmol) in HMPA (5 mL) was added. The reaction mixture was stirred under irradiation by a 150-W tungsten lamp at 15–20 °C for 2 h, and then sodium bromide (3.1 g, 30 mmol) was added to the reaction mixture and heated at 130–140 °C for 4 h. After the usual workup, distillation gave **14a**, 0.98 g (63% yield).

The following compounds were prepared by this procedure.

14b: bp 111 °C (8 mmHg); IR (neat) 1690, 1620 cm^{-1}; NMR (CCl_4) δ 0.97 (3 H, t, J = 7.5 Hz), 1.27 (3 H, t, J = 7.5 Hz); 1.44–1.78 (6 H, m), 2.06–2.46 (6 H, m), 4.10 (2 H, q, J = 7.5 Hz); MS 196 (M^+).

14c: bp 120 °C (48 mmHg); IR (neat) 1690, 1620 cm^{-1}; NMR (CCl_4) δ 0.9 (3 H, m), 1.20 (4 H, m), 1.24 (3 H, t, J = 7.5 Hz), 1.76 (3 H, s), 1.91 (3 H, s), 2.18 (2 H, m), 4.09 (2 H, q, J = 7.5 Hz); MS 184 (M^+).

14d: bp 120 °C (8 mmHg); IR (neat) 1700, 1620 cm^{-1}; NMR (CCl_4) δ 0.95 (3 H, m), 1.26 (3 H, t, J = 7.5 Hz), 1.0–1.4 (6 H, m), 1.4–1.7 (6 H, m), 2.0–2.4 (6 H, m), 4.10 (2 H, q); MS 224 (M^+).

14e: bp 110 °C (2.6 mmHg); IR (neat) 1690, 1620 cm^{-1}; NMR (CCl_4) δ 1.15 (3 H, t), 1.86 (3 H, s), 2.08 (3 H, s), 3.67 (3 H, s), 4.06 (2 H, q), 7.15 (5 H, m); MS 218 (M^+).

14f: 109 °C (12 mmHg); IR (neat) 1740, 1665 cm^{-1}; NMR (CCl_4) δ 1.88 (3 H, s), 2.21 (3 H, s), 2.85 (2 H, m), 4.20 (2 H, q, J = 7.5 Hz); MS 126 (M^+).

14g: bp 116 °C (12 mmHg); IR (neat) 1760, 1670 cm^{-1}; NMR (CCl_4) δ 1.47 (2 H, d, J = 7.0 Hz), 1.86 (3 H, s), 2.20 (3 H, m), 2.80 (2 H, m), 4.50 (1 H, m); MS 140 (M^+).

15a: bp 90 °C (20 mmHg); IR (neat) 1690, 1610 cm^{-1}; NMR (CCl_4) δ 0.99 (3 H, t, J = 7.5 Hz), 1.70 (6 H, d), 2.10 (3 H, s), 2.20 (2 H, q, J = 7.5 Hz); MS 126 (M^+). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.90; H, 11.33.

15b: bp 95 °C (18 mmHg); IR (neat) 1690, 1610 cm^{-1}; NMR (CCl_4) δ 0.95 (3 H, m), 1.08–1.47 (6 H, m), 1.72 (3 H, s), 1.74 (3 H, s), 2.18 (2 H, m), 2.08 (3 H, s); MS 144 (M^+).

15c: bp 85 °C (11 mmHg); IR (neat) 1700, 1610 cm^{-1}; NMR (CCl_4) δ 1.80 (3 H, s), 2.15 (3 H, s), 1.9–2.1 (4 H, m), 2.5 (2 H, m); MS 124 (M^+).

Preparation of β-Acetyl Nitro Compounds (10, 11). Coupling Reaction of Ethyl 2-Acetylbutyrate (5a) with 2a: Preparative Work. A solution of ethyl 2-acetylbutyrate (**5a**, 3.48 g, 22 mmol) in Me_2SO (10 mL) was added to a stirred suspension of t-BuOK (2.46 g, 22 mmol) in Me_2SO (20 mL) at room temperature under nitrogen, and then a solution of 2-chloro-2-nitropropane (**2a**, 2.6 g, 20 mmol) in Me_2SO (10 mL) was added to the reaction mixture. The reaction mixture was irradiated by a 150-W tungsten lamp and then worked up in the usual way to give **10a**, 3.5 g (72% yield); bp 105 °C (0.2 mmHg) [lit.[4b] 153–155 °C (13 mmHg)]; NMR (CCl_4) δ 0.95 (3 H, t, J = 7 Hz), 1.31 (3 H, t, J = 7 Hz), 1.62 (6 H, s), 1.8 (2 H, m), 2.2 (3 H, s), 4.20 (2 H, q, J = 7 Hz). The same reaction was carried out in Me_2SO or DMF with t-BuOK, NaH, or MeOLi as a base under the conditions shown in Table IV and the yield of **10a** was determined by GLC. The results are summarized in Table IV.

Coupling Reaction of 2-Acetylcyclopentanone (6c) with 2a: Preparative Work. A solution of 2-acetylcyclopentanone (**6c**, 1.3 gm, 10 mmol) in Me_2SO (5 mL) was added to a stirred suspension of t-BuOK (1.1 g, 10 mmol) in Me_2SO (20 mL) at room temperature under nitrogen, and then a solution of **2a** (1.3 g, 10 mmol) in Me_2SO (5 mL) was added. The reaction mixture was stirred at room temperature under irradiation by a 150-W tungsten lamp and worked up in the usual way to give **11c**, 1.6 g (75% yield); mp 22–23 °C; IR (KBr) 1740, 1710, 1550 cm^{-1}; NMR (CCl_4) δ 1.57 (3 H, s), 1.88 (3 H, s), 1.8–2.8 (6 H, m), 2.17 (3 H, s). Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09; N, 6.57. Found: C, 56.15; H, 7.30; N, 6.42. This reaction was also carried out by using t-BuOK, NaH, or MeOLi as a base in Me_2SO or THF under the conditions shown in Table IV. The yield of **11c** was determined by GLC with dimethyl malonate as an internal standard.

The following β-acetyl nitro compounds (**10** and **11**) were prepared by using t-BuOK as a base.

10b: bp 120 °C (1 mmHg); IR (neat) 1720, 1710, 1540 cm^{-1}; NMR (CCl_4) δ 0.95 (3 H, t, J = 7 Hz), 1.1–1.4 (4 H, m), 1.32 (3 H, t, J = 7 Hz), 1.8 (2 H, m), 2.20 (3 H, s), 4.20 (2 H, q, J = 7 Hz). Anal. Calcd for $C_{13}H_{23}NO_4$: C, 57.13; H, 8.48; N, 5.13. Found: C, 56.98; H, 8.25; N, 5.10.

10c: IR (neat) 1725, 1710, 1545 cm^{-1}; NMR (CCl_4) δ 1.20 (3 H, t, J = 7 Hz), 1.72 (3 H, s), 1.77 (3 H, s), 2.20 (3 H, s), 3.25 (2 H, s), 4.05 (2 H, q, J = 7 Hz), 7.12 (5 H, m). Anal. Calcd for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.81; H, 6.60; N, 4.52.

11b: bp 124–126 °C (0.3 mmHg); IR (neat) 1700, 1540 cm^{-1}; NMR (CCl_4) δ 0.92 (3 H, m), 1.0–1.6 (6 H, m), 1.66 (6 H, s), 2.09 (6 H, s). Anal. Calcd for $C_{18}H_{21}NO_4$: C, 59.24; H, 8.70; N, 5.76. Found: C, 59.12; H, 8.96; N, 5.68.

11d: mp 76 °C (lit.[4b] 78 °C); NMR (CCl_4) δ 1.58 (3 H, s), 1.66 (6 H, s), 2.10 (6 H, s).

Elimination of the Nitro and Acetyl Groups from 10 or 11. Typical Procedure: Preparation of 2-Methyl-3-ethoxycarbonyl-2-heptene (14c). To a stirred solution of **10c** (2.6 g, 10 mmol) in EDA (50 mL) was added a small piece of Li wire (76 mg, 11 mmol) at room temperature under nitrogen, and the mixture was stirred for 4 h. The reaction mixture was poured into water and extracted with ether. The organic layer was washed with 2 N HCl and water, dried with magnesium sulfate, and concentrated. Distillation of the residue gave **14c**: 1.2 g (66% yield), bp 103 °C (18 mmHg). IR and NMR spectra of this product were identical with those of the compound obtained by the method of eq 6.

Compounds **14a** and **14e** were prepared by the same procedure.

14e: IR (neat) 1690, 1620 cm^{-1}; NMR (CCl_4) δ 1.15 (3 H, t, J = 7 Hz), 1.86 (3 H, s), 2.08 (3 H, s), 3.67 (2 H, s), 4.06 (2 H, q, J = 7 Hz), 7.16 (5 H, m); MS 218 (M^+).

Preparation of α-Isopropylidenecyclopentanone (15c). A solution of **11c** (1.5 g, 7 mmol) in HMPA (5 mL) was added to a stirred solution of the lithium salt of 2-nitropropane (2.0 g, 21 mmol) at room temperature under nitrogen and stirred for 5 h with exposure to a 150-W tungsten lamp. After the usual workup, distillation of the crude product gave **15c**: 0.68 g (78% yield); bp 85 °C (11 mmHg); IR and NMR spectra were in good agreement with those of **15c** prepared by the method of eq 6. Compounds **15b** and **15d** were also prepared by this method. The spectroscopic data of **15b** were identical with those of **15b** prepared by the method of eq 6.

15d: bp 57 °C (49 mmHg); IR (neat) 1680, 1610 cm^{-1}; NMR (CCl_4) δ 1.73 (3 H, s), 1.81 (6 H, s), 2.10 (3 H, s); MS 112 (M^+).

Preparation of α,β-Unsaturated Sulfones (16). Typical Procedure: Preparation of 2-Tosyl-3-methyl-2-butene (16a). A solution of ethyl 2-tosylpropionate (**7a**, 2.8 g, 11 mmol) in Me_2SO (5 mL) was added to a stirred suspension of t-BuOK (1.2 g, 11

mmol) in Me_2SO (20 mL) at room temperature under nitrogen and then a solution of **2a** (1.3 g, 10 mmol) in Me_2SO (5 mL) was added. The reaction mixture was irradiated by a 150-W tungsten lamp for 5 h and then worked up in the usual way. Column chromatography (silica gel/benzene) gave pure **12a**: 2.7 g (80% yield); mp 58–59 °C; IR (KBr) 1740, 1550, 1330, 1160 cm^{-1}; NMR ($CDCl_3$) δ 1.16 (3 H, t, J = 7.5 Hz), 1.60 (3 H, s), 1.92 (3 H, s), 2.24 (3 H, s), 2.46 (3 H, s), 4.00 (2 H, q, J = 7.5 Hz), 7.24 (2 H, d, J = 8.0 Hz), 7.60 (2 H, d, J = 8.0 Hz). Anal. Calcd for $C_{15}H_{21}O_6NS$: C, 52.49; H, 6.16; N, 4.08. Found: C, 52.30; H, 6.38; N, 3.84.

Compounds **12b** and **12c** were prepared by a similar procedure.

12b: mp 83–84 °C; IR (KBr) 1720, 1545, 1310, 1150 cm^{-1}; NMR ($CDCl_3$) δ 0.94 (3 H, t, J = 7.5 Hz), 1.25 (3 H, t, J = 7.5 Hz), 2.03 (3 H, s), 2.21 (3 H, s), 2.25 (2 H, m), 2.45 (3 H, s), 4.16 (2 H, m), 7.34 (2 H, d, J = 8.0 Hz), 7.73 (2 H, d, J = 8.0 Hz). Anal. Calcd for $C_{16}H_{24}O_6NS$: C, 53.77; H, 6.49; N, 3.92. Found: C, 53.89; H, 6.60; N, 3.99.

12c: liquid; IR (neat) 1730, 1540, 1320, 1150 cm^{-1}; NMR ($CDCl_3$) δ 1.04 (6 H, m), 1.54 (1.5 H, s), 1.71 (1.5 H, s), 1.90 (1.5 H, s), 2.20 (1.5 H, s), 2.34 (1 H, q, J = 7.5 Hz), 2.48 (3 H, s), 2.71 (1 H, q, J = 7.5 Hz), 3.98 (2 H, m), 7.31 (2 H, d, J = 8.0 Hz), 7.73 (2 H, d, J = 8.0 Hz). Anal. Calcd for $C_{16}H_{23}O_6NS$: C, 53.77; H, 6.49; N, 3.92. Found: C, 53.87; H, 6.63; N, 3.95.

A mixture of **12a** (2.31 g, 6.75 mmol) and NaBr (2.08 g, 20.2 mmol) in HMPA (20 mL) was heated at 130–40 °C for 2 h. After the usual workup, column chromatography (silic gel/methylene chloride) gave **16a**: 1.3 g (87% yield); mp 60.5–61.5 °C; IR (KBr) 1610, 1290, 1140 cm^{-1}; NMR ($CDCl_3$) δ 1.88 (3 H, s), 1.89 (3 H, m), 2.22 (3 H, m), 2.42 (3 H, s), 7.28 (2 H, d, J = 8.0 Hz), 7.72 (2 H, d, J = 8.0 Hz). Anal. Calcd for $C_{12}H_{16}SO_2$: C, 64.25; H, 7.19. Found: C, 64.16; H, 7.08.

16b: mp 42–43 °C; IR (KBr) 1620, 1295, 1145 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (3 H, t, J = 7.5 Hz), 1.88 (3 H, s), 2.12 (3 H, s), 2.41 (3 H, s), 2.45 (2 H, q, J = 7.5 Hz), 7.27 (2 H, d, J = 8.0 Hz), 7.70 (2 H, d, J = 8.0 Hz). Anal. Calcd for $C_{13}H_{18}SO_2$: C, 65.51; H, 7.61. Found: C, 65.38; H, 7.58.

16c: liquid; IR (neat) 1625, 1300, 1145 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (3 H, t, J = 7.5 Hz), 2.00 (3 H, m), 2.08 (3 H, m), 2.42 (3 H, s), 2.65 (2 H, m), 7.30 (2 H, d, J = 8.0 Hz), 7.72 (2 H, d, J = 8.0 Hz). Anal. Calcd for $C_{13}H_{18}SO_2$: C, 65.51; H, 7.61. Found: C, 65.77; H, 7.47.

Stereochemistry of Elimination. Preparation of Ethyl 1-Cyano-1-benzyl-2-nitro-2-methylvalerate (8i). A solution of ethyl 2-cyano-2-benzylacetate (**3i**, 4.4 g, 22 mmol) in Me_2SO (5 mL) was added to a stirred suspension of NaH (22 mmol) in Me_2SO (30 mL) at room temperature under nitrogen, and then a solution of **1a** (4.0 g, 22 mmol) in Me_2SO (5 mL) was added. The reaction mixture was stirred for 4 h and worked up in the usual way to give **8i** (5.5 g, 82% yield), which consisted of two isomers (**A** and **B**). The ratio of **A**/**B** was determined by HPLC (silica gel/H_2O–MeOH) to reveal that the ratio of **A**/**B** was 57/43. Compounds **8k**, **8l**, **8m**, and **8n** were prepared by the similar methods, and the isomer ratio was determined by HPLC.

Conversion of 8 to 13. A mixture of **8i** (1.3 g, 4.28 mmol) and NaBr (1.32 g, 12.8 mmol) in HMPA (30 mL) was heated at 130–140 °C for 1 h. After the usual workup, distillation of the crude product gave 2-cyano-3-methyl-1-phenyl-2-pentene (**13i**): 0.58 g (73% yield); bp 60–62 °C (1 mmHg); IR (neat) 2220, 1630 cm^{-1}; NMR (CCl_4) δ 1.12 (3 H, m), 1.82 (CH_3—C=C, s, Z isomer), 2.05 (CH_3—C=C, s, E isomer), 2.16–2.40 (2 H, m), 3.46 (2 H, s), 7.20 (5 H, m). The E/Z ratio was determined by the ratio of methyl protons at δ 1.82 and 2.05. Compounds **8k**, **8l**, **8m**, and **8n** were also converted to olefins **13k**, **13l**, **13m**, and **13n** by the same procedure, respectively. NMR data are summarized below, by which E/Z ratio of olefins are determined.

13k: δ 0.95 (3 H, m), 1.50 (2 H, m), 1.80 (CH_3—C=C, s, Z isomer), 2.02 (CH_3—C=C, s, E isomer), 2.2–2.4 (2 H, m), 3.44 (2 H, s), 7.20 (5 H, m).

13l: δ 0.95 (3 H, m), 1.2–1.5 (4 H, m), 1.80 (CH_3C=C, s, Z), 2.0 (CH_3C=C, s, E), 2.2–2.4 (2 H, m), 3.42 (2 H, s), 7.20 (5 H, m).

13m: δ 0.95 (3 H, m), 1.2–1.5 (6 H, m), 1.80 (CH_3C=C, s, Z), 2.05 (CH_3C=C, s, E), 2.2–2.4 (2 H, m), 3.44 (2 H, s), 7.20 (5 H, m).

13n: δ 1.10 (6 H, d, J = 8 Hz), 1.68 (CH_3C=C, s, Z), 1.90 (CH_3C=C, E), 2.5–2.9 (1 H, m), 3.45 ($PhCH_2$, s, E), 3.60 ($PhCH_2$, s, Z), 7.20 (5 H, m).

Separation of the Diastereomers of 8i. Column chromatography (silica gel/benzene) of **8i** was repeated to give pure **8i-A** and **8i-B**.

8i-A: mp 120 °C; IR (KBr) 2240, 1735, 1540 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (3 H, t, J = 7 Hz), 1.16 (3 H, t, J = 7.5 Hz), 1.80 (3 H, s), 2.9 (2 H, m), 3.40 (2 H, m), 4.00 (2 H, q, J = 7.5 Hz), 7.24 (5 H, m). Anal. Calcd for $C_{16}H_{20}N_2O_4$: C, 63.14; H, 6.62; N, 9.20. Found: C, 62.88; H, 6.75; N, 9.28.

8i-B: liquid; IR (neat) 2240, 1735, 1540 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (3 H, t, J = 7.0 Hz), 1.16 (3 H, t, J = 7.5 Hz), 1.82 (3 H, s), 2.20 (2 H, m), 3.24 (2 H, m), 4.10 (2 H, q, J = 7.5 Hz), 7.24 (5 H, m). Anal. Calcd for $C_{16}H_{20}N_2O_4$: C, 63.14; H, 6.62; N, 9.20. Found: C, 63.46; H, 6.75; N, 9.04.

Preparation of Pure (Z)-13i and (E)-13i. A mixture of **8i-A** (0.4 g, 1.3 mol) and sodium bromide (0.4 g, 4 mmol) in HMPA (10 mL) was heated at 130–140 °C for 1 h. The usual workup gave pure (*Z*)-**13i**; NMR (CCl_4) δ 1.14 (3 H, t, J = 7.5 Hz), 1.82 (3 H, s), 2.40 (2 H, q, J = 7.5 Hz), 3.46 (2 H, s), 7.20 (5 H, m). (*E*)-**13i** was prepared from **8i-B** by a similar procedure; NMR (CCl_4) δ 1.10 (3 H, t, J = 7.5 Hz), 2.05 (3 H, s), 2.30 (2 H, q, J = 7.5 Hz), 3.46 (2 H, s), 7.20 (5 H, m).

Registry No. **1a**, 5447-97-2; **1** (R^1 = Me; R^2 = Et), 55653-00-4; **1** (R^1 = R^2 = $(CH_2)_5$), 29788-20-3; **2a**, 594-71-8; **2** (R^1 = R^2 = $(CH_2)_5$), 873-92-7; **3a**$^-$Na$^+$, 87070-09-5; **3i**$^-$Na$^+$, 82650-42-8; **3**$^-$ (R^3 = n-C_4H_9) Na$^+$, 87070-10-8; **3**$^-$ (R^3 = n-C_8H_{17}) Na$^+$, 87070-11-9; **4a**$^-$Na$^+$, 18995-13-6; **4**$^-$ (R^3 = n-C_4H_9; Y = COOEt) Na$^+$, 22600-93-7; **4**$^-$ (R^3 = CH_2Ph; Y = COOEt) Na$^+$, 35472-53-8; **5a**$^-$K$^+$, 81699-60-7; **5a**$^-$Na$^+$, 34292-13-2; **5a**$^-$Li$^+$, 87070-12-0; **5**$^-$ (R^3 = n-C_4H_9; Y = COMe) Na$^+$, 62519-95-3; **5**$^-$ (R = n-C_4H_9; Y = COOEt) K$^+$, 87070-13-1; **5**$^-$ (R = CH_2Ph; Y = COOEt) K$^+$, 87070-14-2; **6c**$^-$K$^+$, 87070-15-3; **6c**$^-$Na$^+$, 87070-16-4; **6c**$^-$Li$^+$, 87070-17-5; **6**$^-$ (R = n-C_4H_9; Y = COMe) K$^+$, 87070-18-6; **6**$^-$ (R = Me; Y = COMe) K$^+$, 72610-66-3; **7a**$^-$K$^+$, 87070-19-7; **8a**, 87070-20-0; **8i-A**, 87070-21-1; **8i-B**, 87070-22-2; **8k-A**, 87070-23-3; **8k-B**, 87070-24-4; **8l-A**, 87070-25-5; **8l-B**, 87070-26-6; **8m-A**, 87070-27-7; **8m-B**, 87070-28-8; **8n-A**, 87070-29-9; **8n-B**, 87070-30-2; **9a**, 75376-77-1; **10a**, 34916-40-0; **10b**, 74479-36-0; **10c**, 87070-31-3; **11b**, 87070-32-4; **11c**, 74479-37-1; **11d**, 34916-41-1; **12a**, 67275-03-0; **12b**, 77218-66-7; **12c**, 77218-65-6; **13a**, 60307-51-9; (*E*)-**13b**, 60307-52-0; (*Z*)-**13b**, 60307-53-1; **13c**, 53153-78-9; **13d**, 60307-54-2; **13e**, 74479-32-6; **13f**, 60307-55-3; **13g**, 87070-33-5; **13h**, 60307-56-4; (*E*)-**13i**, 60307-57-5; (*Z*)-**13i**, 60307-58-6; **13j**, 60307-59-7; (*E*)-**13k**, 87070-34-6; (*Z*)-**13k**, 87070-35-7; (*E*)-**13l**, 87070-36-8; (*Z*)-**13l**, 87070-37-9; (*E*)-**13m**, 87070-38-0; (*Z*)-**13m**, 87070-39-1; (*E*)-**13n**, 87070-40-4; (*Z*)-**13n**, 87070-41-5; **14a**, 18804-45-0; **14b**, 62479-69-0; **14c**, 13979-35-6; **14d**, 62479-70-3; **14e**, 87070-42-6; **14f**, 24186-31-0; **14g**, 87070-43-7; **15a**, 22287-11-2; **15b**, 62479-71-4; **15c**, 2758-17-0; **16a**, 71964-06-2; **16b**, 87070-44-8; **16c**, 87070-45-9.