equivalent bond lengths is 0.6 kcal/mol more stable when CI is included. The MNDO calculated MOs resulting from the ten p AOs in **54e** are split energetically into a characteristic aromatic pattern, comprising one low energy and two sets of doubly degenerate bonding orbitals (Table IX).

In conclusion, in-plane and radial cyclic conjugation of p orbitals in hydrocarbons is predicted. The alternate cyclic radially conjugated 6- and 10-electron systems show aromaticity by all criteria employed (Table VIII). When corrected for strain effects, the stabilization energies due to radial ("in-plane") aromaticity often are 8 kcal/mol or so. In contrast, the $4n$-electron systems, although otherwise similar in structure, show a destabilizing effect of small magnitudes. Although the nonalternate conjugated systems are stable isomers, they are nonaromatic.

Of additional interest are other large spherical unsaturated carbon molecules, several of which have been observed in the gas phase.[37] In particular, the truncated icosahedral C_{60} molecule has been predicted to have a large, stabilizing, delocalization energy.[38] An interesting $C_{20}H_{10}$ polyene, topologically similar to dodecahedrapentene (**54e**), has been suggested by Kornilov.[39]

Acknowledgment. This work was supported by ARRADCOM, Dover, NJ, and by the Fonds der Chemischen Industrie. We thank Christian Schade and Prof. W. Maier for their interest and discussions.

Registry No. **8**, 696-86-6; **9**, 6053-74-3; **10**, 66081-13-8; **11**, 4736-48-5; **12**, 91266-48-7; **24**, 104374-23-4; **25**, 104374-24-5; **26**, 104374-25-6; **27**, 104374-26-7; **28**, 104374-27-8; **29**, 20454-87-9; **30**, 104374-28-9; **31**, 85850-64-2; **32**, 104374-29-0; **32a**, 104374-30-3; **33**, 104374-31-4; **33a**, 104374-32-5; **34**, 104374-33-6; **35**, 104374-34-7; **35a**, 104374-35-8; **35b**, 104374-36-9; **35c**, 104374-37-0; **36**, 63127-44-6; **37**, 104374-38-1; **37a**, 104374-39-2; **37b**, 104374-40-5; **38**, 104374-41-6; **38a**, 104374-42-7; **38b**, 104374-43-8; **38c**, 104374-44-9; **39**, 104374-45-0; **39a**, 104374-46-1; **39b**, 104374-47-2; **39c**, 104374-48-3; **39d**, 104374-49-4; **40**, 104374-50-7; **40a**, 104374-51-8; **40b**, 104374-52-9; **40c**, 104374-53-0; **40d**, 104374-54-1; **40e**, 104374-55-2; **40f**, 104374-56-3; **40g**, 104374-57-4; **41**, 104374-58-5; **41a**, 104374-59-6; **41b**, 104374-60-9; **41c**, 104374-61-0; **41e**, 104374-62-1; **41f**, 104374-63-2; **42**, 104374-64-3; **43**, 104374-65-4; **43a**, 104374-66-5; **43b**, 104374-67-6; **44**, 104374-68-7; **44a**, 104374-69-8; **44b**, 104374-70-1; **44c**, 104374-71-2; **44d**, 104374-72-3; **45**, 104374-73-4; **45a**, 104393-12-6; **46**, 104374-74-5; **46a**, 104374-75-6; **46b**, 104374-76-7; **46c**, 104374-77-8; **46d**, 104374-78-9; **47**, 104374-79-0; **47a**, 104374-80-3; **48**, 104374-81-4; **49**, 4493-23-6; **50**, 77159-24-1; **51**, 104374-82-5; **51a**, 104374-83-6; **51b**, 104374-84-7; **51c**, 104374-85-8; **51d**, 104374-86-9; **52**, 104374-87-0; **52a**, 104374-88-1; **52b**, 104374-89-2; **52c**, 104374-90-5; **52d**, 104374-91-6; **52e**, 104374-92-7; **52f**, 104374-93-8; **52g**, 104374-94-9; **52h**, 104374-95-0; **52i**, 104374-96-1; **52j**, 104374-97-2; **52k**, 104374-98-3; **53**, 104374-99-4; **53a**, 104375-00-0; **53b**, 104375-01-1; **53c**, 104375-02-2; **53d**, 104375-03-3; **53e**, 104375-04-4; **53f**, 104375-05-5; **53g**, 104375-06-6; **53h**, 104375-07-7; **53i**, 104375-08-8; **53j**, 104375-09-9; **53k**, 104375-10-2; **53m**, 104375-11-3; **53n**, 104375-12-4; **54**, 104375-13-5; **54a**, 104375-14-6; **54b**, 104375-15-7; **54c**, 104375-16-8; **54d**, 104375-17-9; **54e**, 104375-18-0; **54f**, 104375-19-1; **54g**, 104375-20-4; **54h**, 104375-21-5; **54i**, 104375-22-6; **54j**, 104375-23-7; **5jk**, 104375-24-8; **5jl**, 104375-25-9; **54m**, 104375-26-0; **54n**, 104375-27-1; **55**, 104375-28-2; **55a**, 104375-29-3; **55c**, 104375-30-6; **55d**, 104375-31-7; **55e**, 104375-32-8; **55f**, 104375-33-9; **55g**, 104375-34-0; **55h**, 104375-35-1; **55i**, 104375-36-2; **56**, 104375-37-3; **56a**, 104375-38-4; **56b**, 104375-39-5; **56c**, 104375-40-8; **57**, 53129-39-8; **57a**, 104375-41-9; **57b**, 104375-42-0; **57c**, 104375-43-1; **58**, 104375-44-2; **59**, 104375-45-3; **60**, 60606-97-5; **61**, 104375-46-4; **61a**, 104375-47-5; **62**, 104375-48-6; **62a**, 104375-49-7; **63**, 104375-50-0; **64**, 104375-51-1; **64a**, 104375-52-2; **64b**, 104375-53-3; **65**, 104375-54-4; **65a**, 104375-55-5.

(37) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779; *Chem. Eng. News* **1985**, *63*(51), 20. Bloomfield, L. A.; Geusic, M. E.; Freemen, R. R.; Brown, W. L. *Chem. Phys. Lett.* **1985**, *121*, 33. Cox, D. M.; Trevor, D. J.; Reichmann, K. C.; Kaldor, A. *J. Am. Chem. Soc.* **1986**, *108*, 2457. Liu, Y.; O'Brien, S. C.; Zhang, Q.; Heath, J. R.; Tittel, F. K.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *Chem. Phys. Lett.* **1986**, *126*, 215. Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Phys. Chem.* **1986**, *90*, 525.

(38) Haymet, A. D. J. *J. Am. Chem. Soc.* **1986**, *108*, 319. Klein, D. J.; Schmatz, T. G.; Hite, G. E.; Seitz, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 1301. Newton, M. D.; Stanton, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 2469. Stone, A. J.; Wales, D. J. *Chem. Phys. Lett.* **1986**, *128*, 501. Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459. Disch, R. L.; Schulman, J. M. *Chem. Phys. Lett.* **1986**, *125*, 465.

(39) Karnilov, M. V. *Dokl. Akad. Nauk. Ukran. SSSR* **1977**, 1097.

Facile Synthesis of Allylic Nitro Compounds by *N,N*-Dimethylethylenediamine-Catalyzed Condensation of Aliphatic and Alicyclic Ketones with Primary Nitroalkanes

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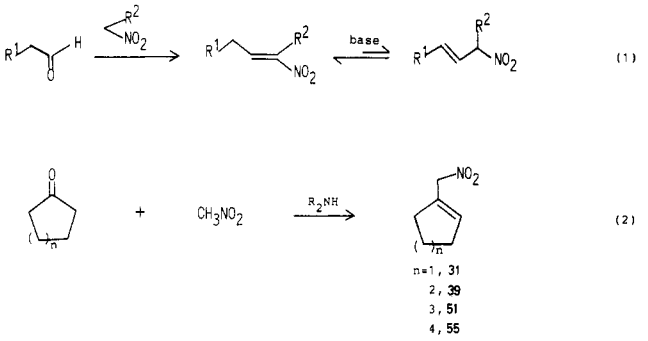
Aliphatic as well as alicyclic ketones condense with primary nitroalkanes in the presence of *N,N*-dimethylethylenediamine (**1**) to give allylic nitro compounds selectively in good to excellent yields without forming α-nitro olefins. Condensation of 2-alkanones and 2-methylcyclopentanone with nitromethane produces the products of thermodynamic control, while the product of kinetic control is obtained from 2-methylcyclohexanone. Propiophenone, an aromatic ketone, reacted with nitromethane in a way analogous to aliphatic ketones to give the corresponding allylic nitro product. A reaction mechanism to account for the exclusive formation of allylic nitro compounds is proposed. Some allylic nitro compounds thus obtained are converted into α,β-unsaturated aldehydes and ketones by treatment with sodium methoxide and then $TiCl_3$ in a buffered solution.

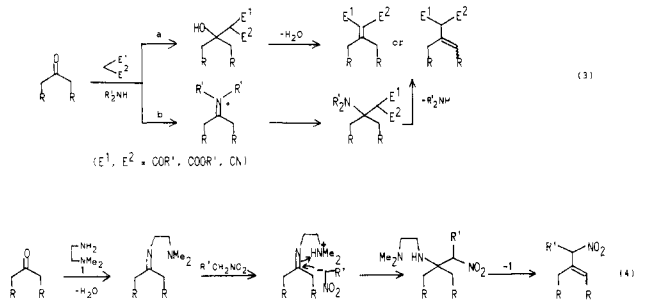
The use of allylic compounds for carbon–carbon bond formation and for functionality transformation has been the subject of considerable recent development. Allylic nitro compounds are particularly versatile intermediates in that they can react both as nucleophiles and electrophiles.[1-3] In addition, the nitro group is readily trans-

0022-3263/86/1951-4368$01.50/0

Scheme I



Scheme II



formed into other functional groups such as carbonyl or amino groups.[4] In spite of this synthetic versatility, the limited accessibility of allylic nitro compounds has severely restricted their utilization for organic synthesis. For example, conversion of allylic halides to allylic nitro compounds by displacement with nitrite ion is not practical because of the ambident character (N vs. O attack) of the nitrite anion.[5] In principal, isomerization of α-nitro olefins, available from the condensation of aldehydes with nitroalkanes (Scheme I, eq 1) to the allylic isomer under basic conditions should provide ready access to this desirable class of compounds. Such is indeed the case: we have shown that isomerization of α-nitro olefins to the allylic isomer occurs by taking advantage of equilibration of the two isomers under basic conditions.[2] However, with respect to the condensation of ketones with nitroalkanes (the Knoevenagel condensation), despite considerable efforts, only nitromethane is reported to condense with five- to eight-membered cycloalkanones under the influence of secondary amine to give directly 1-(nitromethyl)cycloalkenes, allylic nitro compounds (Scheme I, eq 2).[6-8] There has been no successful report of condensation of aliphatic ketones with nitroalkanes to give α-nitro olefins and/or allylic nitro compounds.[6-8]

Table I. Amine-Catalyzed Condensation of 3-Pentanone with Nitromethane[a]

entry	amine (mol %)	4, yield,[b] %
1	piperidine (30)	4
2	piperidine (30) + AcOH (150)	2
3	cyclohexylamine (30)	27
4	$H_2N(CH_2)_3NH_2$ (30)	55
5	$H_2N(CH_2)_2NH_2$ (30)	55
6	$MeNH(CH_2)_2NHMe$ (30)	2
7	$H_2N(CH_2)_2NMe_2$ (10) + 1	39
8	1 (20)	60
9	1 (30)	83
10	cyclohexylamine (30) + Et_3N (30)	21

[a] See general procedure A in Experimental Section. (b) Yields were determined by GLC using an internal standard.

In order to extend our studies on transition-metal-catalyzed allylation reactions of allylic nitro compounds,[2] we have been exploring general synthetic procedures for allylic nitro compounds and have focused our attention on the hitherto unexplored condensation of aliphatic and alicyclic ketones with nitroalkanes.

In general, two mechanisms for the amine-catalyzed Knoevenagel condensation have been proposed (Scheme II, eq 3).[8,9] In one of them, the amine catalyst serves only as a base to generate an enolate anion of an active methylene compound, which then adds to the ketone. This is followed by dehydration in a similar fashion to the Claisen–Schmit reaction (path a). The other involves the formation of a Schiff base and subsequent addition of the enolate anion to form an intermediate amino compound, followed by elimination of the amine (path b). Compared with the facile Knoevenagel condensation of active methylene compounds with ketones, the lack of generality in the case of nitroalkanes is mainly ascribed to the lower nucleophilicity of the nitro-stabilized carbanion, resulting in undesired side reactions. We envisioned that, in general, the use of a primary amine as a catalyst should favor the path involving the Schiff base intermediate and, furthermore, the use of *N,N*-dimethylethylenediamine (**1**) bearing both primary and tertiary amino moieties within the same molecule should promote the addition of nitroalkanes to the Schiff base intermediate as depicted in eq 4.[10]

In this paper, we report the results of condensation of alicyclic and aliphatic ketones with primary nitroalkanes to yield allylic nitro compounds by using **1** as the condensing reagent. Further, we demonstrate transformations of the newly obtained allylic nitro compounds into synthetically valuable α,β-unsaturated aldehydes and ketones.

Results

Condensation of Aliphatic Ketones with Nitroalkanes. We speculated that choice of catalyst was critical for successful condensation. In order to find the most suitable catalyst, condensation of 3-pentanone (**2**) with nitromethane (**3**) was studied by using various amine catalysts in refluxing benzene with removal of the water formed in the reaction by azeotropic distillation (eq 5). As shown in Table I, diamines were more suitable bases than

(1) (a) Buckley, G. D.; Charlish, J. L. *J. Chem. Soc.* **1947**, 1472–1474. (b) Grob, C. A.; von Tscharner, W. *Helv. Chim. Acta* **1950**, *33*, 1070–1079. (c) Lehr, F.; Gonnermann, J.; Seebach, D. *Helv. Chim. Acta* **1979**, *62*, 2258–2275.

(2) (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. *Tetrahedron Lett.* **1985**, *26*, 851–854. (d) Tamura, R.; Hayashi, K.; Kakihana, M.; Tsuji, M.; Oda, D. *Chem. Lett.* **1985**, 229–232.

(3) (a) Ono, N.; Hamamoto, I.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1982**, 821–822. (b) Ono, N.; Hamamoto, I.; Kaji, A. *Ibid.* **1984**, 274–275. (c) Ono, N.; Hamamoto, I.; Yanai, T.; Kaji, A. *Ibid.* **1985**, 523–524. (d) Ono, N.; Hamamoto, I.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1863–1864.

(4) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1–18.

(5) Kornblum, N. *Org. React. (N.Y.)* **1962**, *12*, 101–156.

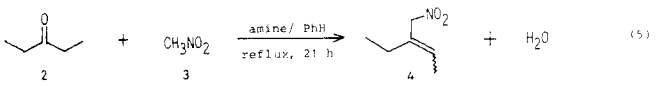
(6) *Houben-Weyl. Methoden der Organischen Chemie*, 4th ed.; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1971; Vol. X, Part 1, pp 336–338.

(7) Bear, H. H.; Urbas, L. In *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H., Ed.; Interscience Publishers: New York, 1970; Part 2, pp 112–115.

(8) Jones, G. *Org. React. (N.Y.)* **1967**, *15*, 204–599

(9) Huose, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin, Ind.: Menlo Park, CA, 1972; pp 646–653.

(10) 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.



primary and secondary monoamines. Particularly, the use of **1** led to improved yields of the condensation product **4**, whereas the simultaneous use of primary and tertiary monoamines had little effect (entry 10). When 4 equiv of **3** and 0.3 equiv of **1** to **2** were employed, the best yield (83%) of **4**, as a mixture of *E* and *Z* isomers, was obtained (entry 9). The *E* and *Z* stereochemistry was assigned by proton NOE measurement. The irradiation of nitromethylene protons at δ 4.85 (*E*) and δ 4.98 (*Z*) resulted in a clean increase (14% after correction) of integration of the olefin proton signal at δ 5.72 for the *E* isomer and a negligible increase for the *Z* isomer, respectively. The *E*/*Z* ratio was 82:18 on the basis of the ^{1}H NMR integration of the two nitromethylene protons.

It is noteworthy that although the aliphatic α-nitro olefin is considered to be much more stable than the corresponding allylic isomer owing to its conjugated structure, the condensation product was exclusively the allylic nitro compound. Formation of neither the α-nitro olefin nor 1,3-dinitro-2,2-dimethylpropane, from addition of another molecule of **3** to the resulting α-nitro olefin in the reaction catalyzed by secondary amines, was observed.[11]

Table II lists examples of condensation of aliphatic ketones with **3** and nitroethane (**5**) to give allylic nitro compounds exclusively. The reaction is quite sensitive to steric bulk of both the nitroalkanes and the ketones. The reaction of **2** with **5** gave **6** in only 24% yield (entry 2). The condensation of ketones bearing methyl groups at the α or β positions with **3** resulted in poor yields (entries 4 and 6). This low reactivity due to steric hindrance was somewhat improved by using a large excess of **3** and 1 equiv of **1** with ketones (entries 3, 5, and 7). Entries 6–13 illustrate the high selectivity for the position of the double bond with respect to 2-alkanones, giving internal olefins exclusively. Even propiophenone (**20**), an aromatic ketone, reacted with **3** in a way analogous to aliphatic ketones by using **1** to produce allylic nitro compound **21** (entry 14). Acetophenone (**22**), acetylacetone (**24**), and methyl acetoacetate (**26**), however, failed to give condensation products with **3**, but instead the stable Schiff bases were obtained in high yields in each case (entries 15–17). The pyrrole derivative **29** was produced in 94% yield as a single product from 2,5-hexanedione (**28**) (entry 18). In these unsuccessful cases, no effect was noted when a large excess of **3** and 1 equiv of **1** to ketones were used, nor even when the reaction was run for longer periods of time at an elevated temperature (110 °C).

Condensation of Alicyclic Ketones with Nitroalkanes. The use of **1** has a certain advantage over that of monoamines and other ethylenediamine derivatives: great improvement in yields of condensation products was observed in most cases as shown in Table III. The reaction conditions were optimized in the reaction of cyclohexanone **38** with **5**. The best yield (80%) of **40** was obtained by using 4 equiv of **5** and 0.3 equiv of **1** to **38** (entry 6).

A 84:16 mixture of allylic nitro compound **32** and α-nitro olefin **33** was obtained in the condensation of cyclopentanone (**30**) with **5** (entry 2), whereas only allylic isomers were formed in other examples. 2-Methylcyclopentanone (**35**) was condensed with **3** to give a 18:82 mixture of two allylic isomers, in which the thermodynamically stable **37** was predominant over **36** (entry 4). On the contrary, exposure of 2-methylcyclohexanone (**42**) to the same reaction conditions gave the product **43** of kinetic control exclusively (entry 8). When 3-methylcyclohexanone (**45**) was used, the product **46** was predominantly obtained (entry 10).

From α-tetralone (**48**), the desired product **49** was obtained in 72% yield, but 1-indanone (**34**) was incompatible

Chart I

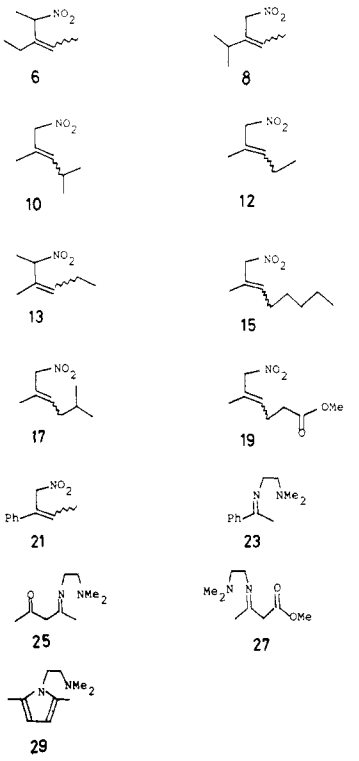
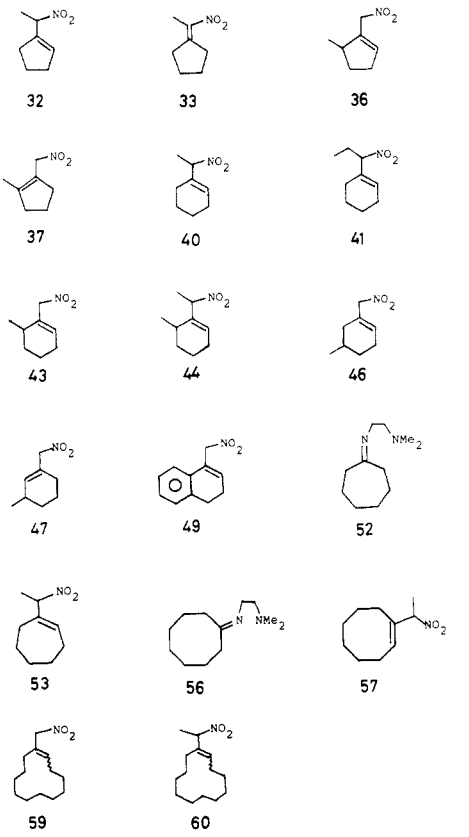


Chart II



(11) (a) Smiley, R. A.; Pritchett, W. A. *J. Chem. Eng. Data* **1966**, *11*, 617–618. (b) Lambert, A.; Lowe, A. *J. Chem. Soc.* **1947**, 1517–1519.

Table II. Condensation of Aliphatic Ketones with Nitroalkanes[a]

entry	ketone	nitroalkane (equiv)	time, h	product	E/Z[b]	yield[c] %
1	**2**	**3** (4.0)	21	**4**	82/18	80
2	**2**	**5** (4.0)	24	**6**	10/90	24
3	**2**	**5** (10.0)	95	**6**	10/90	55[d]
4	$Me_2CHCOCH_2CH_3$ (**7**)	**3** (4.0)	22	**8**	34/66	24
5	**7**	**3** (10.0)	96	**8**	29/71	38[d]
6	$MeCOCH_2CHMe_2$ (**9**)	**3** (4.0)	24	**10**	74/26	30
7	**9**	**3** (10.0)	51	**10**	75/25	59[d]
8	$MeCO(CH_2)_2Me$ (**11**)	**3** (4.0)	18	**12**	74/26	78
9	**11**	**5** (10.0)	96	**13**	21/79	20[d]
10	$MeCO(CH_2)_5Me$ (**14**)	**3** (4.0)	48	**15**	72/28	50
11	**14**	**3** (10.0)	12	**15**	73/27	70
12	$MeCO(CH_2)_2CHMe_2$ (**16**)	**3** (10.0)	8.5	**17**	78/22	73
13	$MeCO(CH_2)_3COOMe$ (**18**)	**3** (10.0)	24	**19**	71/29	55
14	$PhCOCH_2Me$ (**20**)	**3** (4.0)	24	**21**	47/53	80
15	PhCOMe (**22**)	**3** (4.0)	24	**23**		79[d]
16	$MeCOCH_2COMe$ (**24**)	**3** (4.0)	**72**	**25**		98[d]
17	$MeCOCH_2COOMe$ (**26**)	**3** (4.0)	72	**27**		91[d]
18	$MeCO(CH_2)_2COMe$ (**28**)	**3** (4.0)	72	**29**		94[d]

[a] General procedure B. [b] Determined by ^1H NMR. [c] Isolated yield. [d] One equivalent of **1** to the ketone was used.

with the reaction conditions employed due to its thermal instability (entries 11 and 3).

Although condensation of **38** with **5** and 1-nitropropane or that of **42** with **3** proceeded smoothly (entries 6–8), the reaction of **42** with **5** was slow (entry 9). Apparently the reaction is susceptible to steric inhibition. Cycloheptanone (**50**), -octanone (**54**), and -dodecanone (**58**) were easily condensed with **3** under the above optimum conditions to give good to excellent yields of products (entries 12, 15, and 18), but the reactions with **5** became so slow that the corresponding Schiff bases were produced as the major products (entries 13 and 16). This poor reactivity, also explained in terms of steric inhibition, was improved by using a large excess of **5** and 1 equiv of **1** to ketones in latter cases (entries 14, 17, and 19).

Attempts to get the condensation products from 1,2- and 1,4-cyclohexanediones and **3** were unsuccessful, giving only intractable tars.

Transformations into α,β-Unsaturated Aldehydes and Ketones. Some of the allylic nitro compounds thus, obtained (Tables II and III) were converted to α,β-unsaturated aldehydes and ketones by treatment with sodium methoxide and then a buffered $TiCl_3$ solution.[12] Results are summarized in Table IV. In entry 1, sodium methoxide in methanol was replaced by potassium *tert*-butoxide in tetrahydrofuran to obtain the anion of **32** efficiently, because the use of methoxide caused the isomerization of **32** to **33** and subsequent addition of methanol to **33**, lowering the yield of **61**. Treatment of the anions of allylic nitro compounds consisting of a mixture of *E* and *Z* isomers with $TiCl_3$ resulted in the formation of conjugated aldehydes with high stereoselectivity (entries 7–9).

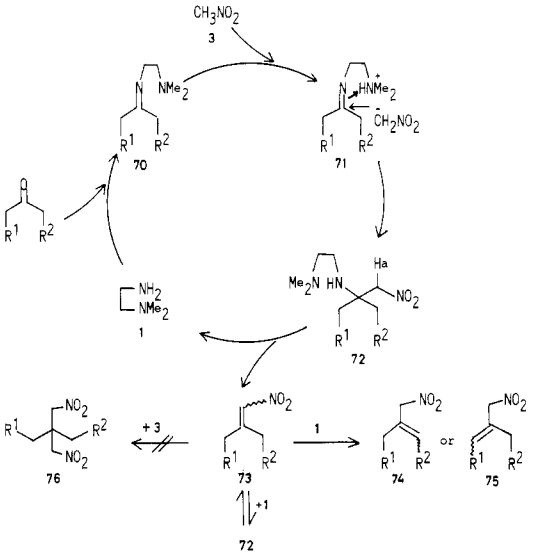
This procedure offers a facile synthetic route to conjugated aldehydes and ketones by one or more carbon homologation of alicyclic and aliphatic ketones.

Discussion

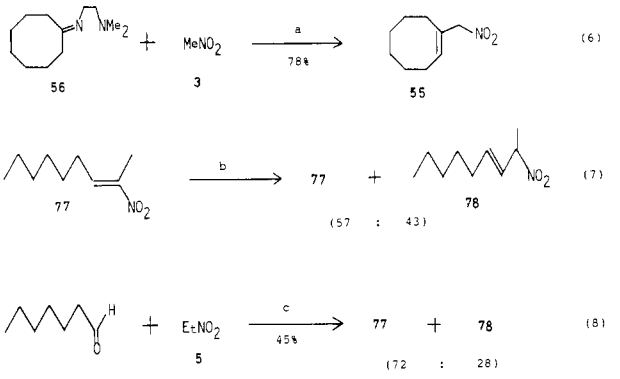
The condensation of ketones with **3** in the presence of **1** can be explained by the following mechanism (Scheme III). Ketone is condensed with **1** to form the Schiff base **70**. The dimethylamino group in **70** behaves as a base to bring **3** close to **70** and then to pick up the active hydrogen of **3**. Nucleophilic addition of the carbanion of **3** to the imino group in **71** gives **72**. Next the dimethylamino group in **72** again serves as a base to abstract proton Ha, resulting in the elimination of **1** and the formation of α-nitro olefin **73**. This α-nitro olefin undergoes 1-catalyzed isomerization to give either the allylic nitro product **74** of thermodynamic control or the product **75** of kinetic control. Fortunately, addition of another molecule of **3** to **73** did not occur.[11] The reaction with **5** and 1-nitropropane would proceed in accordance with the above mechanism.

In order to verify this proposed mechanism, the reaction of the Schiff base **56**, prepared from **54** and **1** (entry 16 in

Scheme III



Scheme IV[a]



[a] (a) PhH, reflux, 18 h; (b) **1**, PhH, reflux, 24 h; (c) **1**, PhH, reflux, 1 h.

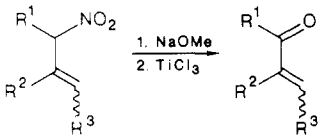
(12) (a) McMurry, J. E.; Melton, J. *J. Org. Chem.* **1973**, *38*, 4367–4373. (b) Ho, T.-L.; Wong, C. M. *Synthesis* **1974**, 196–197.

Table III. Condensation of Alicyclic Ketones with Nitroalkanes[a]

entry	ketone	nitroalkane (equiv)	time, h	product	yield,[b] %
1	cyclopentanone (**30**)	**3** (4.0)	3.5	**31**	61 (22)[c]
2	**30**	**5** (4.0)	24	**32** + **33** (84:16)[d]	73
3	1-indanone (**34**)	**3** (4.0)	24		0
4	2-methylcyclopentanone (**35**)	**3** (4.0)	48	**36** + **37** (18:32)[d]	45
5	cyclohexanone (**38**)	**3** (4.0)	6	**39**	76 (55)[c]
6	**38**	**5** (4.0)	21	**40**	80 (0)[c] (18)[e]
7	**38**	n-$C_3H_7NO_2$ (4.0)	22	**41**	75
8	2-methylcyclohexanone (**42**)	**3** (4.0)	4	**43**	87 (8)[c]
9	**42**	**5** (10.0)	24	**44**	22
10	3-methylcyclohexanone (**45**)	**3** (4.0)	5	**46** + **47** (68:32)[d]	79 (30)[c]
11	α-tetralone (**48**)	**3** (10.0)	96	**49**	72
12	cycloheptanone (**50**)	**3** (4.0)	6	**51**	70 (60)[c]
13	**50**	**5** (4.0)	22	**52**	73[f]
14	**50**	**5** (10.0)	13	53	82[f]
15	cyclooctanone (**54**)	**3** (4.0)	14	**55**	83 (9)[c]
16	**54**	**5** (4.0)	48	**56**	82[f]
17	**54**	**5** (30.0)	24	**57**	56[f]
18	cyclododecanone (**58**)	**3** (4.0)	22	**59** (E/Z = 73/27)[d]	99 (0)[c]
19	**58**	**5** (30.0)	86	**60** (E/Z = 90/10)[d]	41[f]

[a] General procedure B. [b] Isolated yield. [c] Piperidine (0.3 equiv to the ketone) was used as a base instead of **1**. [d] Determined by ^{1}H NMR. [e] Ethylenediamine (0.3 equiv to the ketone) was used as a base instead of **1**. [f] One equivalent of **1** to the ketone was used.

Table IV. Synthesis of α,β-Unsaturated Aldehydes and Ketones from Allylic Nitro Compounds[a]



entry	allylic nitro compound	R^1	R^2	R^3	product	yield,[b] %
1	**32** + **33**	Me		$(CH_2)_3$	**61**	80[c]
2	**40**	Me		$(CH_2)_4$	**62**	81
3	**43**	H		$-CHMe(CH_2)_3$	**63**	92
4	**52**	Me		$(CH_2)_5$	**64**	60
5	**55** (E)	H		$(CH_2)_6$	**65** (E)[d]	66
6	**57** (E)	Me		$(CH_2)_6$	**66** (E)[d]	40
7	**59** (E/Z = 73/27)	H		$(CH_2)_{10}$	**67** (E)[d]	79
8	**15** (E/Z = 72/28)	H	Me	$(CH_2)_4Me$	**68** (E)[d]	50
9	**21** (E/Z = 47/53)	H	Ph	Me	**69** (Z)[d]	51

[a] General procedure C. [b] Isolated yield. [c] t-BuOK and THF were used instead of MeONa and MeOH. [d] Determined by ^{1}H NMR.

Table III), with 4 equiv of **3** was performed in refluxing benzene. As expected, allylic nitro product **55** was obtained in 78% yield (Scheme IV, eq 6). The condensation of ketones with nitroalkanes using **1** is subject to steric hindrance in both the ketones and the nitroalkanes. These observations and the fact that the Schiff bases are easily produced from **1** and ketones indicate that, in the **1**-catalyzed condensation, addition of nitroalkane to the Schiff base **70** is rate-determining (Scheme III).

The above mechanism can well account for the exclusive formation of allylic nitro compounds in all cases, except one (entry 2 in Table III). To assess the ability of **1** for catalyzing the isomerization of α-nitro olefin **73** to allylic product **74** or **75**, α-nitro olefin **77**, prepared from n-heptanal and **5**, was treated with 0.1 equiv of **1** in refluxing benzene for 24 h (Scheme IV, eq 7). As a result, even from the stable α-nitro olefin, considerable isomerization occurred to afford an equilibrium mixture of **77** and **78** in an ratio of 57:43, which was isolated as the mixture of the same ratio by usual workup. Attempted condensation of n-heptanal with 4 equiv of **5** by using 0.3 equiv of **1** produced the 72:28 mixture of **77** and **78** in 45% yield (eq 8).

When primary monoamines were used instead of **1**, reaction was very slow, probably due to the formation of the stable Schiff base and hence the insufficient concentration of remaining base to generate the carbanion of nitroalkane. Except for a few cases, secondary monoamines also gave poor results. This is attributable to the formation of undesired products such as enamines and oximes of azadispiro keto cyclic hydroxamic acids in the reaction of alicyclic ketones,[7,13] and that of dinitro compounds **76** as major products in the reaction of aliphatic ketones.[11] Among diamines, *N,N'*-dimethylethylenediamine, bearing two secondary amino moieties, was inferior to primary monoamines in yield (entry 6 in Table I). Ethylenediamine was an effective catalyst in some cases but inferior to **1** because both amino groups might be prone to form the Schiff base. Furthermore, the observation that the simultaneous use of primary and tertiary monoamines was not effective (entry 10 in Table I) indicates that the existence of both primary and tertiary amino moieties within one molecule is essential for an efficient reaction.

Experimental Section

General. Infrared spectra were recorded on either a Beckman Model 4200 or a Shimadzu IR-27G spectrophotometer and are reported in cm^{-1}. ^{1}H NMR spectra were measured with either a JEOL FX-90Q (90 MHz) or a Varian XL-300 (300 MHz) instrument using Me_3Si 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). Column chromatography was performed on

(13) (a) Nightingale, D. V.; Miki, S.; Heintz, D. N.; Reich, D. A. *J. Org. Chem.* **1963**, *28*, 642–646. (b) House, H. O.; Magin, R. W. *Ibid.* **1963**, *28*, 647–651. (c) Noland, W. E.; Sundberg, R. J. *Ibid.* **1963**, *28*, 3150–3165.

Merck silica gel 60 (less than 230 mesh) under moderate pressure (3 atm). Elemental analyses were performed by the Kyoto University Microanalytical Laboratories.

Materials. Benzene and methanol were purified by distillation. THF was distilled from sodium benzophenone ketyl. All commercially available ketones, except 1-indanone and cyclododecanone, were purified by distillation before use. 1-Indanone, cyclododecanone, piperidine, cyclohexylamine, ethylenediamine, 1,3-propanediamine, *N,N'*- and *N,N*-dimethylethylenediamine, and triethylamine were commercial samples and were used without further purification. 2-Methylcyclopentanone was prepared by a published procedure.[14] Methyl 5-oxohexanoate was prepared by the NaOMe-catalyzed 1,4-addition of methyl acetoacetate to methyl acrylate in methanol, followed by demethoxycarbonylation (LiCl in aqueous Me_2SO, 160 °C, 4 h,[15] overall yield 73%). 2-Nitro-2-nonene was prepared by a published procedure.[16]

General Procedure A for Condensation of 3-Pentanone (2) and Nitromethane (3) with Various Amine Catalysts (Table I). 2-Ethyl-1-nitro-2-butene (4). In a round-bottomed flask fitted with a Dean and Stark trap was placed **2** (860 mg, 10 mmol), **3** (2.44 g, 40 mmol), the amine catalyst (1.0–3.0 mmol), and benzene (25 mL), and the solution was refluxed for 21 h. Upon cooling, the reaction was monitored by GLC analysis. An analytical pure sample of **4** was obtained according to general procedure B after purification by distillation at 81 °C (17 torr). The ratio of **4E** to **4Z** was 82:18 as judged by ^1H NMR integration of the signals at δ 4.85 and 4.98, respectively.

4: IR (neat) 1668, 1558, 1379 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.72 (q, J = 6.8 Hz, 1 H), [4.98 (s, 2 H) for **4Z**], 4.85 (s, 2 H), 2.21 (q, J = 7.5 Hz, 2 H), 1.72 (d, J = 6.8 Hz, 3 H), 1.01 (t, J = 7.5 Hz, 3 H). Anal. ($C_6H_{11}NO_2$) C, H, N.

General Procedure B for the Preparation of Allylic Nitro Compounds with *N,N*-Dimethylethylenediamine (1). In a round-bottomed flask fitted with a Dean and Stark trap were placed the ketone (20 mmol), the nitroalkane (80 mmol–0.6 mol), **1** (6–20 mmol), and benzene (50 mL), and the solution was refluxed until ca. 0.36 mL of water was collected. The benzene solution was cooled, washed with aqueous 2 N HCl solution (20 mL) and water (20 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo. Products were purified by distillation, except for **60** which was isolated by column chromatography (4:1 hexane–ethyl acetate).

(*E*)- and (*Z*)-3-Ethyl-2-nitro-3-pentene (6): E/Z = 10/90; bp 90 °C/14 torr; IR (neat) 1693, 1550, 1386, cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.73 (q, J = 7.0 Hz, 1 H), 5.03 (2 q, J = 7.0 Hz, 1 H), [4.39 (2 q, J = 7.0 Hz, 1 H) for **6E**], 2.14 (q, J = 7.6 Hz, 2 H), 1.70 (d, J = 7.0 Hz, 3 H), 1.61 (d, J = 7.0 Hz, 3 H), 0.99 (t, J = 7.6 Hz, 3 H). Anal. ($C_7H_{13}NO_2$) C, H, N.

(*E*)- and (*Z*)-2-Isopropyl-1-nitro-2-butene (8): E/Z = 29/71; bp 91 °C/16 torr; IR (neat) 1660, 1548, 1383 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.81 (q, J = 7.0 Hz, 1 H), [5.73 (q, J = 7.0 Hz, 1 H) for **8E**], 4.99 (s, 2 H), [4.82 (s, 2 H) for **8E**], [3.09–2.60 (m, 1 H) for **8E**], 2.59–2.00 (m, 1 H), 1.75 (d, J = 7.0 Hz, 3 H), 1.04 (d, J = 6.8 Hz, 6 H), [1.02 (d, J = 7.4 Hz, 6 H) for **8E**]. Anal. ($C_7H_{13}NO_2$) C, H, N.

(*E*)- and (*Z*)-2,4-Dimethyl-1-nitro-2-pentene (10): E/Z = 75/25; bp 91 °C/17 torr; IR (neat) 1643, 1550, 1380 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.45 (d, J = 9.5 Hz, 1 H), [4.96 (s, 2 H) for **10Z**], 4.79 (s, 2 H), 2.57 (m, J = 9.5, 6.6 Hz, 1 H), 1.82 (s, 3 H), [1.77 (s, 3 H) for **10Z**], 0.99 (d, J = 6.6 Hz, 6 H). Anal. ($C_7H_{13}NO_2$) C, H, N.

(*E*)- and (*Z*)-2-Methyl-1-nitro-2-pentene (12): E/Z = 74/26; bp 83–84 °C/17 torr; IR (neat) 1670, 1554, 1380 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.64 (t, J = 7.1 Hz, 1 H), [4.95 (s, 2 H) for **12Z**], 4.81 (s, 2 H), 2.12 (dq, J = 7.7, 7.1 Hz, 2 H), 1.85 (s, 3 H), [1.75 (s, 3 H) for **12Z**], 1.00 (t, J = 7.7 Hz, 3 H). Anal. ($C_6H_{11}NO_2$) C, H, N.

(*E*)- and (*Z*)-3-Methyl-2-nitro-3-hexene (13): E/Z = 21/79; bp 83 °C/14 torr; IR (neat) 1550, 1388 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.62 (t, J = 7.0 Hz, 1 H), 4.98 (q, J = 6.8 Hz, 1 H), [4.42 (q, J = 7.3 Hz, 1 H) for **13E**], 2.09 (dq, J = 7.0, 7.5 Hz, 2 H), 1.67 (s, 3 H), 1.66 (d, J = 6.8 Hz, 3 H), 0.99 (t, J = 7.5 Hz, 3 H). Anal. ($C_7H_{13}NO_2$) C, H, N.

(*E*)- and (*Z*)-2-Methyl-1-nitro-2-octene (15): E/Z = 73/27; bp 118 °C/12 torr; IR (neat) 1554, 1379 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.65 (t, J = 7.3 Hz, 1 H), [4.95 (s, 2 H) for **15Z**], 4.82 (s, 2 H) 2.07 (dt, J = [illegible]3, 7.7 Hz, 2 H), 1.85 (s, 3 H), [1.75 (s, 3 H) for **15Z**], 1.60–1.06 [illegible]r m, 6 H), 0.89 (t, J = 6.6 Hz, 3 H). Anal. ($C_9H_{17}NO_2$) C, H, N.

(*E*)- and (*Z*)-2,5-Dimethyl-1-nitro-2-hexene (17): E/Z = 78/22; bp 100–101 °C/13 torr; IR (neat) 1553, 1376 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.67 (t, J = 7.0 Hz, 1 H), [4.95 (s, 2 H) for **17Z**], 4.83 (s, 2 H), 2.00 (dd, J = 7.0, 7.2 Hz, 2 H), 1.88 (s, 3 H), [1.75 (s, 3 H) for **17Z**], 1.83–1.31 (m, 1 H), 0.91 (d, J = 6.4 Hz, 6 H). Anal. ($C_8H_{15}NO_2$) C, H, N.

(*E*)- and (*Z*)-Methyl 5-methyl-6-nitro-4-hexenoate (19): E/Z = 71/29; bp 89–90 °C/0.10 torr; IR (neat) 1738, 1553, 1383 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.59 (t, J = 7.7 Hz, 1 H), [5.01 (s, 2 H) for **19Z**], 4.83 (s, 2 H), 3.68 (s, 3 H), 2.63–2.09 (m, 2 H), 2.54–2.37 (br, 2 H), 1.86 (s, 3 H), [1.80 (s, 3 H) for **19Z**]. Anal. ($C_8H_{13}NO_4$) C, H, N.

(*E*)- and (*Z*)-1-Nitro-2-phenyl-2-butene (21): E/Z = 47/53; bp 86–87 °C/0.10 torr; IR (neat) 1650, 1550, 1378 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.51–6.97 (m, 5 H), 6.39 (q, J = 7.0 Hz, 1 H), [6.13 (q, J = 6.8 Hz, 1 H) for **21E**], 5.45 (s, 2 H), [5.19 (s, 2 H) for **21E**], 2.01 (d, J = 7.0 Hz, 3 H), [1.78 (d, J = 6.8 Hz, 3 H) for **21E**]. Anal. ($C_{10}H_{11}NO_2$) C, H, N.

1-(Nitromethyl)cyclopentene (31): bp 78.5 °C/12.5 torr; IR (neat) 1542 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.91 (br, 1 H), 5.01 (s, 2 H), 2.75–2.27 (br m, 4 H), 2.27–1.62 (br m, 2 H). Anal. ($C_6H_9NO_2$) C, H, N.

1-(1-Nitroethyl)cyclopentene (32) and 1-(nitroethylidene)cyclopentane (33): bp 104–105 °C/16 torr [The ratio of **32** to **33** was 84:16 as judged by ^1H NMR integration of the signals for the methyl groups at δ 1.68 and 1.94, respectively.]; IR (neat) 1665, 1550, 1390 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (br, 1 H), 5.21 (q, J = 6.9 Hz, 1 H), 2.44–2.32 (br m, 4 H), [2.19 (m, 4 H) for **33**], 1.99–1.89 (m, 2 H), [1.94 (s, 3 H) for **33**], [1.81–1.74 (m, 4 H) for **33**], 1.68 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 138.9, 132.0, 83.0, 32.4, 31.8, 23.1, 17.6, [154.7, 140.0, 34.6, 34.5, 27.0, 25.7, 16.0 for **33**]. Anal. ($C_7H_{11}NO_2$) C, H, N.

5- and 2-methyl-1-(nitromethyl)cyclopentene (36 and 37): Kugelrohr distillation 120–125 °C/13 torr [The ratio of **36** to **37** was 18:82 as judged by ^1H NMR integration of the olefin proton signal of **36** at δ 5.89 and the signal for the nitromethylene protons of **36** and **37** at 4.98.]; IR (neat) 1680, 1553, 1382 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ [5.89 (br, 1 H) for **36**], 4.98 (s, 2 H), 2.60–2.03 (br m, 4 H), 2.01–1.42 (br m, 2 H), 1.77 (s, 3 H), [1.07 (d, J = 6.8 Hz, 3 H) for **36**]; ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 144.1, 124.9, 74.0, 38.7, 35.0, 21.6, 14.0, [138.0, 135.3, 74.6, 41.0, 32.8, 31.0, 18.7 for **36**]. Anal. ($C_7H_{11}NO_2$) C, H, N.

1-(Nitromethyl)cyclohexene (39): bp 109 °C/14 torr; IR (neat) 1669, 1549 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.07 (br, 1 H), 4.90 (s, 2 H), 2.44–2.27 (br m, 4 H), 2.27–1.42 (br m, 4 H). Anal. ($C_7H_{11}NO_2$) C, H, N.

1-(1-Nitroethyl)cyclohexene (40): bp 122.5 °C/19 torr; IR (neat) 1665, 1546, 1385 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.92 (br, 1 H), 4.97 (q, J = 6.8 Hz, 1 H), 2.23–1.86 (br m, 4 H), 1.86–1.43 (br m, 4 H), 1.61 (d, J = 6.8 Hz, 3 H). Anal. ($C_8H_{13}NO_2$) C, H, N.

1-(1-Nitropropyl)cyclohexene (41): bp 62 °C/0.08 torr; IR (neat) 1662, 1550, 1380 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.92 (br, 1 H), 4.73 (t, J = 7.5 Hz, 1 H), 2.47–1.83 (br m, 4 H), 1.83–1.26 (br m, 4 H), 1.86 (dt, J = 7.5, 7.0 Hz, 2 H), 0.92 (t, J = 7.0 Hz, 3 H). Anal. ($C_9H_{15}NO_2$) C, H, N.

6-Methyl-1-(nitromethyl)cyclohexene (43): bp 114 °C/14 torr; IR (neat) 1660, 1550, 1375 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.92 (t, J = 0.9 Hz, 1 H), 4.97 (d, J = 12.9 Hz, 1 H), 4.70 (d, J = 12.9 Hz, 1 H), 2.50–1.89 (br m, 3 H), 1.89–1.27 (br m, 4 H), 1.06 (d, J = 6.8 Hz, 3 H). Anal. ($C_8H_{13}NO_2$) C, H, N.

6-Methyl-1-(1-nitroethyl)cyclohexene (44): bp 112 °C/14 torr. For the mixture of two diastereoisomers: IR (neat) 1660, 1550, 1385 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 5.96 (t, J = 3.9 Hz, 1 H), [5.83 (t, J = 3.9 Hz, 1 H) for the minor diastereoisomer], 5.03 (q, J = 6.4 Hz, 1 H), [4.96 (q, J = 6.4 Hz, 1 H) for the minor diastereoisomer], 2.49–1.83 (br m, 3 H), 1.83–1.23 (br m, 4 H),

(14) Edwards, H. N.; Wycpalek, A. F.; Corbin, N. C.; McChesney, J. D. *Synth. Commun.* **1978**, *8*, 563–567.
(15) Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* **1973**, 957–960.
(16) Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*, 2138–2139.

1.61 (d, J = 6.4 Hz, 3 H), [1.60 (d, J = 6.4 Hz, 3 H), 1.11 (d, J = 6.8 Hz, 3 H) for the minor diastereoisomer], 1.04 (d, J = 6.8 Hz, 3 H). Anal. ($C_9H_{15}NO_2$) C, H, N.

5- and 3-Methyl-1-(nitromethyl)cyclohexene (46 and 47): bp 116 °C/13 torr. The ratio of **46** to **47** was 68:32 as judged by ^{1}H NMR integration of the olefin proton signals at δ 5.92 and 5.77, respectively. For the mixture: IR (neat) 1667, 1546, 1375 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92 (br, 1 H), [5.77 (br, 1 H) for **47**], 4.79 (s, 2 H), 2.36–2.00 (br m, 4 H), 1.90–1.50 (br m, 3 H), [1.20 (d, J = 7.2 Hz, 3 H) for **47**], 0.99 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 132.7, 128.0, 82.6, 35.1, 29.7, 28.4, 25.4, 21.4, [138.9, 128.3, 82.7, 30.3, 29.7, 26.7, 21.2, 21.0 for **47**]. Anal. ($C_8H_{13}NO_2$) C, H, N.

1-(Nitromethyl)-3,4-dihydronaphthalene (49): bp 116 °C/0.02 torr; IR (neat) 1680, 1560, 1373 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 4 H), 6.29 (t, J = 4.6 Hz, 1 H), 5.25 (s, 2 H), 2.84 (t, J = 8.1 Hz, 2 H), 2.42 (dt, J = 4.6, 8.1 Hz, 2 H). Anal. ($C_{11}H_{11}NO_2$) C, H, N.

1-(Nitromethyl)cycloheptene (51): bp 126 °C/15 torr; IR (neat) 1670, 1549 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.10 (t, J = 6.0 Hz, 1 H), 4.85 (s, 2 H), 1.58–2.00 (br m, 4 H), 2.00–1.25 (br m, 6 H). Anal. ($C_8H_{13}NO_2$) C, H, N.

1-(1-Nitroethyl)cycloheptene (53): bp 57 °C/0.06 torr; IR (neat) 1665, 1545, 1390 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.02 (t, J = 6.4 Hz, 1 H), 4.96 (q, J = 6.8 Hz, 1 H), 2.63–1.99 (br m, 4 H), 1.99–1.29 (br m, 6 H), 1.60 (d, J = 6.8 Hz, 3 H). Anal. ($C_9H_{15}NO_2$) C, H, N.

1-(Nitromethyl)cyclooctene (55): bp 65 °C/0.15 torr; IR (neat) 1672, 1559, 1381 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.90 (t, J = 7.5 Hz, 1 H), 4.85 (s, 2 H), 2.54–2.06 (br m, 4 H), 1.80–1.26 (br m, 8 H). Anal. ($C_9H_{15}NO_2$) C, H, N.

1-(1-Nitroethyl)cyclooctene (57): bp 63 °C/0.03 torr; IR (neat) 1550, 1379 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.87 (t, J = 8.3 Hz, 1 H), 5.02 (q, J = 7.0 Hz, 1 H), 2.43–1.99 (br m, 4 H), 1.81–1.30 (br m, 8 H), 1.63 (d, J = 7.0 Hz, 3 H). Anal. ($C_{10}H_{17}NO_2$) C, H, N.

(*E*)- and (*Z*)-1-(Nitromethyl)cyclododecene (59): E/Z = 73/27; bp 99 °C/0.04 torr; IR (neat) 1655, 1550, 1375 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ [5.86 (t, J = 7.7 Hz, 1 H) for **59Z**], 5.64 (t, J = 7.7 Hz, 1 H), [5.01 (s, 2 H) for **59Z**], 4.86 (s, 2 H), 2.40–2.00 (br m, 4 H), 1.71–0.94 (br m, 16 H). Anal. ($C_{13}H_{23}NO_2$) C, H, N.

1-(1-Nitroethyl)cyclododecene (60): E/Z = 90/10; IR (neat) 1551, 1388 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ [5.80 (t, J = 7.7 Hz, 1 H) for **60Z**], 5.68 (t, J = 8.0 Hz, 1 H), [5.50 (q, J = 6.8 Hz, 1 H) for **60Z**], 5.60 (q, J = 6.8 Hz, 1 H), 2.51–1.83 (br m, 4 H), 1.76–1.06 (br m, 16 H), 1.64 (d, J = 6.8 Hz, 3 H). Anal. ($C_{14}H_{25}NO_2$) C, H, N.

Isolation of the Schiff Bases. *N*-(1-Phenylethylidene)-*N'*,*N'*-dimethylethylenediamine (23). In a round-bottomed flask fitted with a Dean and Stark trap were placed **22** (1.20 g, 10 mmol), **3** (2.44 g, 40 mmol), **1** (0.88 g, 10 mmol), and benzene (25 mL), and the solution was refluxed. After 24 h, 0.18 mL of water were collected. The benzene solution was cooled and the solvent and **3** were removed in vacuo. Distillation of the resulting oil (63–67 °C/0.05 torr) gave 1.51 g (79%) of **23** as a pale yellow oil.

23: IR (neat) 1634, 1446, 1286 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.83–7.20 (m, 5 H), 3.61 (t, J = 7.3 Hz, 2 H), 2.72 (t, J = 7.3 Hz, 2 H), 2.33 (s, 6 H), 2.23 (s, 3 H). Anal. ($C_{12}H_{18}N_2$) C, H, N.

The following compounds were also prepared by the procedure employed for the isolation of **23**.

***N*-(4-Oxopent-2-ylidene)-*N'*,*N'*-dimethylethylenediamine (25)**: bp 69 °C/0.40 torr; IR (CCl_4) 1613, 1557, 1295 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.97 (s, 1 H), 3.36 (t, J = 6.4 Hz, 1 H), 3.30 (t, J = 6.4 Hz, 1 H), 2.48 (t, J = 6.4 Hz, 2 H), 2.46–2.17 (br, 1 H), 2.27 (s, 6 H), 1.98 (s, 3 H), 1.93 (s, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 194.4, 162.3, 95.1, 58.8, 45.3, 41.1, 28.5, 18.6. Anal. ($C_9H_{18}N_2O$) C, H, N.

***N*-(1-(Methoxycarbonyl)prop-2-ylidene)-*N'*,*N'*-dimethylethylenediamine (27)**: bp 80–81 °C/0.20 torr; IR (neat) 1661, 1601 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.43 (s, 1 H), 3.60 (s, 3 H), 3.33 (t, J = 6.6 Hz, 1 H), 3.26 (t, J = 6.6 Hz, 1 H), 2.46 (t, J = 6.6 Hz, 2 H), 2.40–2.20 (br, 1 H), 2.26 (s, 6 H), 1.93 (s, 3 H). Anal. ($C_9H_{18}N_2O_2$) C, H, N.

***N*-Cycloheptylidene-*N'*,*N'*-dimethylethylenediamine (52)**: bp 53 °C/0.09 torr; IR (neat) 1642, 1548, 1452 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.31 (t, J = 7.5 Hz, 2 H), 2.86–2.06 (br m, 4 H), 2.59 (t, J = 7.5 Hz, 2 H), 2.28 (s, 6 H), 1.89–1.29 (br m, 8 H). Anal. ($C_{11}H_{22}N_2$) C, H, N.

***N*-Cyclooctylidene-*N'*,*N'*-dimethylethylenediamine (56)**: bp 71 °C/0.08 torr; IR (neat) 1650, 1550, 1465 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.45 (t, J = 7.5 Hz, 2 H), 2.58 (t, J = 7.5 Hz, 2 H), 2.89–2.00 (br m, 4 H), 2.29 (s, 6 H), 2.00–1.20 (br m, 10 H). Anal. ($C_{12}H_{24}N_2$) C, H, N.

Isolation of 1-(2-(Dimethylamino)ethyl)-2,5-dimethylpyrrole (29). In a round-bottomed flask fitted with a Dean and Stark trap were placed **28** (1.14 g, 10 mmol), **3** (2.44 g, 40 mmol), **1** (0.88 g, 10 mmol), and benzene (25 mL), and the solution was refluxed. After 72 h 0.36 mL of water was collected. The benzene solution was cooled, and the solvent and **3** were removed in vacuo. Distillation of the resulting oil (60 °C/0.10 torr) gave 1.56 g (94%) of **29** as a pale yellow oil.

29: IR (neat) 1580, 1521, 1464, 1410, 1310, 752 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.73 (br, 2 H), 3.84 (t, J = 8.1 Hz, 2 H), 2.42 (t, J = 8.1 Hz, 2 H), 2.28 (s, 6 H), 2.21 (s, 6 H). Anal. ($C_{10}H_{18}N_2$) C, H, N.

General Procedure C for the Preparation of α,β-Unsaturated Aldehydes and Ketones. 1-Acetylcyclohexene (62). The ketone **62** was made by the procedure of McMurray and Melton.[12] A buffered $TiCl_3$ solution was prepared by adding NH_4OAc (1.84 g, 24 mmol) in H_2O (6 mL) to 20% aqueous $TiCl_3$ (0.62 g, 4.0 mmol, 3.2 mL of H_2O) under argon. This buffered solution was added to a solution of **40** (0.155 g, 1.0 mmol) and sodium methoxide (0.054 g, 1.0 mmol) in methanol (10 mL) and stirred under argon for 1 h at room temperature. The reaction mixture was poured into ether (50 mL) and the aqueous phase was extracted with ether (2 × 30 mL). The organic extracts were combined, washed with 5% $NaHCO_3$ (30 mL) and brine (30 mL), and dried over $MgSO_4$, and the solvent was removed in vacuo. Kugelrohr distillation (150 °C/12 torr) of the resulting oil gave 0.10 g (81%) of **62** as a colorless oil. Its ^{1}H NMR and IR spectral data coincided with those of the authentic sample.[17] Anal. ($C_8H_{12}O$) C, H.

3-Methylcyclohexene-2-carboxaldehyde (63): Kugelrohr distillation 100 °C/13 torr. Its ^{1}H NMR and IR spectral data coincided with those of material prepared by an alternate procedure.[18] Anal. ($C_8H_{12}O$) C, H.

1-Acetylcycloheptene (64): Kugelrohr distillation 110 °C/14 torr; IR (neat) 1670, 1640 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.08 (t, J = 6.6 Hz, 1 H), 2.60–2.23 (br m, 4 H), 2.29 (s, 3 H), 1.97–1.29 (br m, 6 H). Anal. ($C_9H_{14}O$) C, H.

(*E*)-1-Cyclooctene-1-carboxaldehyde (65): Kugelrohr distillation 150 °C/13 torr. Its ^{1}H NMR and IR spectral data coincided with those of material prepared by an alternate procedure.[19] Anal. ($C_9H_{14}O$) C, H.

(*E*)-1-Acetylcyclooctene (66): Kugelrohr distillation 60 °C/0.15 torr; IR (neat) 1668, 1635 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.88 (t, J = 8.2 Hz, 1 H), 2.60–2.19 (br m, 4 H), 2.30 (s, 3 H), 1.86–1.31 (br m, 8 H). Anal. ($C_{10}H_{16}O$) C, H.

(*E*)-1-Cyclododecene-1-carboxaldehyde (67): Kugelrohr distillation 120 °C/0.10 torr. Its ^{1}H NMR and IR spectral data coincided with those of material prepared by an alternate procedure.[20] Anal. ($C_{13}H_{22}O$) C, H.

(*E*)-2-Methyl-2-octenal (68): Kugelrohr distillation 125 °C/14 torr. Its ^{1}H NMR and IR spectral data coincided with those of material prepared by an alternate procedure.[21] Anal. ($C_8H_{16}O$) C, H.

(*Z*)-2-Phenyl-2-butenal (69): Kugelrohr distillation 95 °C/0.1 torr; IR (neat) 1690, 1635, 1600, 1495 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 9.58 (s, 1 H), 7.50–6.91 (m, 5 H), 6.81 (q, J = 7.0 Hz, 1 H), 1.98 (d, J = 7.0 Hz, 3 H). Anal. ($C_{10}H_{10}O$) C, H.

1-Acetylcyclopentene (61). The potassium salt of **32** was prepared by adding the 84:16 mixture of **32** and **33** (0.56 g, 4.0 mmol) to potassium *tert*-butoxide (0.45 g, 4.0 mmol) in THF (25

(17) Aldrich: NMR, 2, 135B; IR, 263B.
(18) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147–154.
(19) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785–2812.
(20) Williams, D. R.; Nishitani, K. *Tetrahedron Lett.* **1980**, *21*, 4417–4420.
(21) Chamberlin, A. R.; Bond, F. T. *Synthesis* **1979**, 44–45.

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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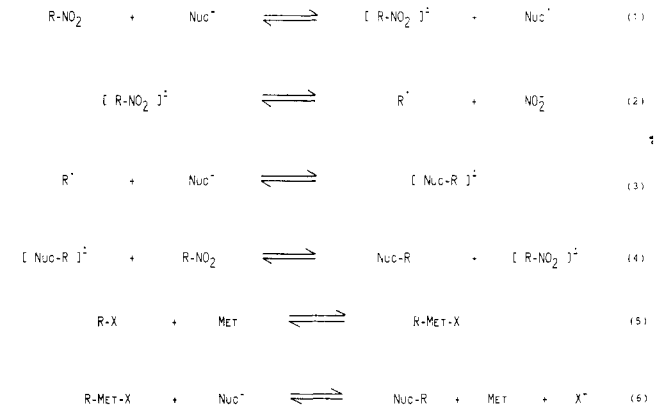
Primary, secondary, and tertiary allylic nitro compounds underwent Pd(0)-catalyzed allylic substitution by stabilized carbanions, secondary amines, and benzenesulfinate ion ($PhSO_2^-$). α,β-Disubstituted α-nitro olefins also behaved as allylic nitro compounds, via base-catalyzed vinyl → allyl rearrangement, 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