Fluorescence Measurements. The steady-state fluorescence measurements were performed in a right-angle geometry with a spectrofluorimeter from SLM; a description of this apparatus has been given in a previous publication.[20]

Laser Flash Photolysis. For laser flash photolysis, excitation was carried out in a front-face configuration with 337.1-nm laser pulses (8 ns, 2–3 mJ) from a Molectron UV-400 system or 425-nm laser pulses (6 ns, 2–10 mJ), generated by pumping a methanolic solution of stilbene 420 (Exciton) with the output at third harmonic (354 nm) from a Quanta-Ray Nd-YAG system. The details of the kinetic spectrometer and computerized data collection system are available elsewhere.[20-22] Rectangular quartz cells with 2- or 3-mm path lengths along the direction of the analyzing light were used for laser flash photolysis. Deoxygenation of solutions was effected by saturating them with argon.

Registry No. **1a**, 2313-03-3; **1a**$^{+\cdot}$, 97861-48-8; **1b**, 97861-35-3; **1b**$^{+\cdot}$, 97861-49-9; **1c**, 97861-36-4; **1c**$^{+\cdot}$, 97861-50-2; **1d**, 97861-37-5; **1d**$^{+\cdot}$, 97861-51-3; **1e**, 6963-25-3; **1e**$^{+\cdot}$, 97877-61-7; **2a**, 97861-38-6; **2a**$^{+\cdot}$, 97861-43-3; **2b**, 97861-39-7; **2b**$^{+\cdot}$, 97877-60-6; **2c**, 97861-40-0; **2c**$^{+\cdot}$, 97861-44-4; **2d**, 92545-46-5; **2d**$^{+\cdot}$, 97877-62-8; **3**, 31994-73-7; **4a**, 5369-56-2; **4b**, 97861-41-1; **4c**, 97861-42-2; **5a**, 65425-10-7; **5b**, 65425-11-8; **5b**$^{+\cdot}$, 97861-45-5; **5c**, 65425-12-9; **5c**$^{+\cdot}$, 97861-46-6; **5d**, 65425-05-0; **5d**$^{+\cdot}$, 97861-47-7; **6**, 3117-37-1; **7a**, 134-81-6; **7b**, 2431-00-7; **7c**, 22711-21-3; **7d**, 39229-12-4; **8**, 98-86-2; **9a**, 5435-97-2; **9b**, 88406-92-2; **9c**, 88406-93-3; **9d**, 88406-95-5; **9e**, 88406-97-7; **10a**, 97861-52-4; **10b**, 97861-53-5; **10c**, 97861-54-6; DCN, 3029-30-9; DCA, 1217-45-4; *t*-BuO·, 3141-58-0; H·, 12385-13-6; *p*-$BrC_6H_4COC(C_6H_5)$=$CHCOC_6H_5$, 97861-56-8; *p*-$CNC_6H_4COC(C_6H_5)$=$CHCOC_6H_5$, 97861-57-9; 3-phenyl-2-benzofuranoxy radical, 97861-55-7.

New Synthetic Methods. Conjugate Addition of Alkyl Groups to Electron Deficient Olefins with Nitroalkanes as Alkyl Anion Equivalents[1]

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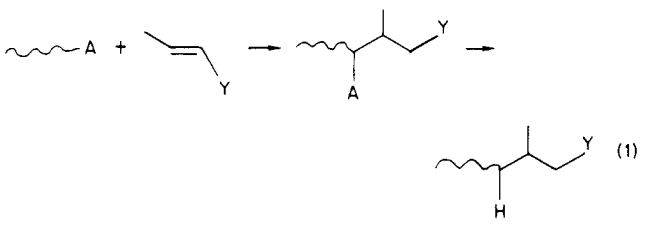
Received May 21, 1985

The sequence of the Michael addition of nitroalkanes and denitration from the adduct provides a new and general method for conjugate addition of primary and secondary alkyl groups to electron deficient olefins such as α,β-unsaturated aldehydes, ketones, esters, nitriles, sulfoxides, and sulfones.

Conjugate addition of alkyl groups to electron deficient olefins is a highly useful reaction as basic strategy for organic synthesis. Although direct addition of organometallics reagents to electron deficient olefins is straightforward, it cannot be applied to all kinds of cases.[2,3] To compensate the defects of the direct method, an indirect method using an activating group, A, as in eq 1 has also been used extensively. As organo sulfur groups stabilize an adjacent carbanion effectively and also they are readily removed, they have been used most frequently among various kinds of A.[4] In this paper we wish to report the nitro group to be the best A in eq 1. Namely, the nitro group stabilizes an adjacent carbanion more effectively and is removed more selectively than any other groups.



(1)

Y=electron withdrawing group
A= SR, SOR, SO_2R, CN, NO_2 etc.

Results and Discussion

A new method for conjugate addition consists of the sequence of two steps, the Michael addition of nitroalkanes and denitration from the adduct. The novelity of a new method lies in the second step, replacement of the nitro group by hydrogen. This type of reaction has been found in recent years,[5] and five methods are available so far.[6] Among them, the method using tributyltin hydride is the only one reliable method to be applied to denitration of the Michael adduct.[7]

Conjugate Addition of Secondary Alkyl Groups. The Michael addition of secondary nitro compounds and the subsequent removal of the nitro group from the adduct provide a new and general method for conjugate addition of secondary alkyl groups to electron deficient olefins (eq 2). The results are summarized in Table I. Three typical examples are selected and shown in eq 3, 4, and 5. The first example is the conjugate addition of the 2-octyl group to methyl vinyl ketone. The first step was simply done by mixing 2-nitrooctane, methyl vinyl ketone, and tetramethylguanidine (TMG, 0.1 equiv)[8] in acetonitrile at room

(1) Preliminary report of this work: Ono, N.; Miyake, H.; Tamura, R.; Kaji, A. *Tetrahedron Lett.* **1981**, *22*, 1705.

(2) (a) Posner, G. H. *Org. React.* **1972**, *19*, 1. (b) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59. (c) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem.* **1982**, *47*, 119. (d) Clive, D. L. J.; Farina, V.; Beaulieu, P. L. *Ibid.* **1982**, *47*, 2572. (e) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Ibid.* **1984**, *49*, 3938.

(3) Although conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds has been well studied, other types of conjugate addition are little known, see ref 2.

(4) (a) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. (b) Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978. (c) Stowell, J. C. "Carbanions in Organic Synthesis"; John Wiley and Sons: New York, 1979.

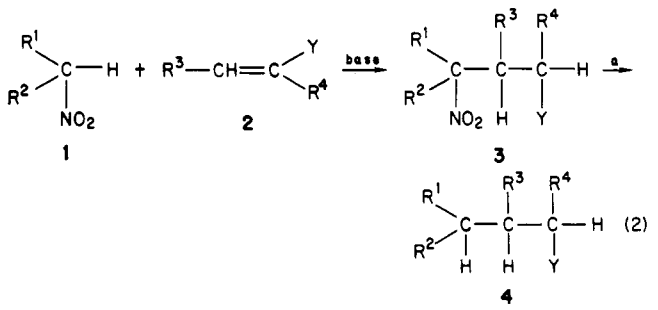
(5) First clean denitrohydrogenation was reported in 1978 by N. Kornblum, where MeSNa was used as a reducing agent: Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 289: *Ibid.* **1979**, *101*, 647.

(6) Method A, the use of MeSNa in dipolar aprotic solvents.[5] Method B, the use of KOH in ethylene glycol: Krasuska, A. L.; Pitrowska, H.; Urbanski, T. *Tetrahedron Lett.* **1979**, 1243. Method, C, the use of 1-benzyl-1,4-dihydronicotinamide: Ono, N.; Tamura, R.; Kaji, A. *J. Am. Chem. Soc.* **1980**, *102*, 2581; *Ibid.* **1983**, *105*, 4017. Method D, the present method using Bu_3SnH.[1] Independently Tanner reported that some kinds of tertiary nitro groups were replaced by hydrogen with Bu_3SnH: Tanner, D. D.; Blackburn, E. V.; Diaz, D. D. *J. Am. Chem. Soc.* **1981**, *103*, 1557. Method E, the use of NaTeH: Suzuki, H.; Takaoka, K.; Osuka, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1067.

(7) The nitro compounds used for denitration in ref 6 were mostly tertiary and activated compounds. In fact it was reported that NaTeH was unable to replace the nitro groups of **3** in Table I by hydrogen.[6] Bu_3SnH is the best reagent so far for replacing the nitro group by hydrogen.[1]

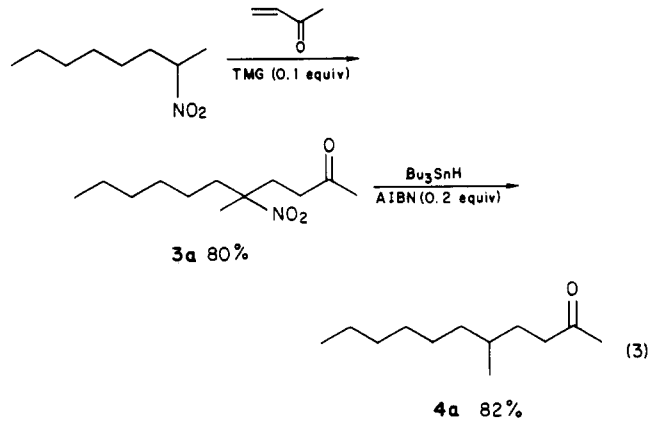
(8) Giuli, D.; Barco, G.; Pollini, G. P. *Synthesis*, **1972**, 45.

0022-3263/85/1950-3692$01.50/0

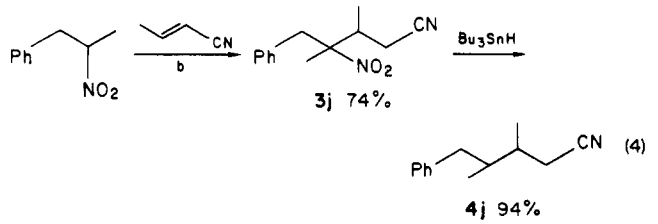


Y = C(=O)R, COOR, CN, CHO, SOR, SO_2R
a, Bu_3SnH(1.2-1.3 equiv), AIBN(0.2 equiv), benzene, 80 °C, 2h

temperature. The adduct, **3a**, was isolated in 80% yield. Heating a mixture of **3a**, Bu_3SnH (1.3 equiv), and azobis(isobutyronitrile) (AIBN, 0.2 equiv) in benzene at 80 °C for 2 h resulted in clean denitration giving **4a** in 82% yield.

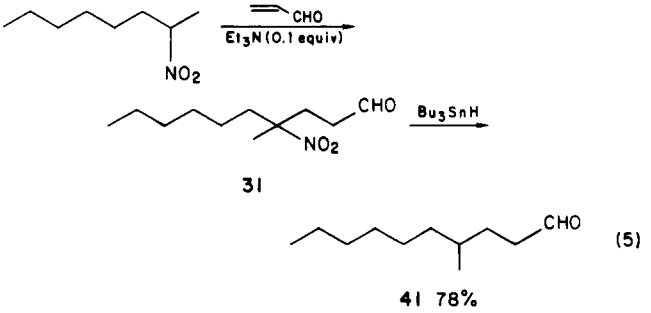


The second example is the conugate addition of secondary alkyl groups to crotononitrile. In general, it is rather difficult to bring about the Michael addition of secondary nitro compounds to α- or β-substituted alkenes or α,β-unsaturated sulfoxides owing to low reactivity of these olefins. This difficulty of the Michael addition is simply resolved by using 1,8-diazabicyclo[5.4.0]undecene-7 (DBU) as a catalyst.[9] The subsequent denitration with Bu_3SnH gave the conjugate addition product to crotononitrile. The sequence of these processes provides a general method for the conjugate addition to less reactive olefins.



b, DBU (1 equiv), CH_3CN, room temp, 24 h

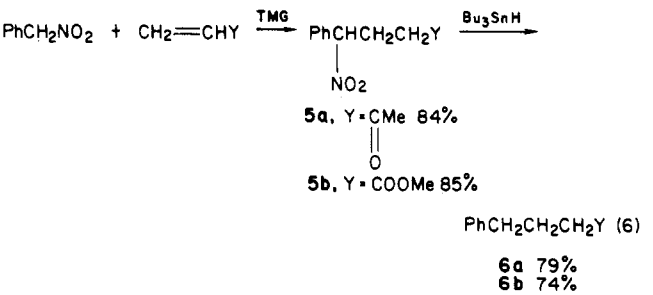
The third example is the conjugate addition of secondary alkyl groups to very reactive olefins such as acrolein (eq 5). The conjugate addition of alkyl groups to very reactive olefins are generally difficult to be accomplished, because such reactive olefins are readily polymerized on treatment with organometallic reagents. However, this problem is not serious in the Michael addition of nitro compounds, for it can be carried out under mild conditions. For example, the reaction of 2-nitrooctane with acrolein proceeds in the presence of catalytic amount of triethylamine and the adduct, **31**, was obtained in 72% yield. Denitration of **31** with Bu_3SnH proceeded without affecting the formyl function to give **41** in 78% yield.



Thus, various olefins are conjugatively alkylated by the method of eq 2. The most important point is that Bu_3SnH can replace the nitro group by hydrogen without affecting other reducible groups such as keto, alkoxycarbonyl, cyano, formyl, sulfinyl, and sulfonyl groups. In this point, the nitro group is evidently superior to other groups as A in eq 1, because it is almost impossible to remove A without affecting Y when A and Y are organosulfur groups.

Although some of **4** can be alternatively prepared by the direct addition of RMgX or R_2CuLi to **2**, a lot of difficulties are generally encountered in most cases. For example, the reagents, RMgX + CuX, R_2CuLi, RCu, RCu + BF_3·OEt_2, and $R_2Cu(CN)Li_2$ do not undergo the conjugate addition to α,β-unsaturated nitriles, but do the 1,2-addition to give the corresponding ketones mainly.[10] The reaction of α,β-unsaturated sulfoxides with organometallic reagents also gives the corresponding sulfides in most cases.[11,12] As discussed already, the conjugate addition of RMgX or R_2CuLi to reactive olefins such as methyl vinyl ketone, acrolein, and methyl acrylate is also not a simple reaction.[13] These difficulties accompanied with the conventional direct addition are now simply resolved by the present method.

Conjugate Addition of Primary Alkyl Groups. The conjugate addition of primary alkyl groups by this method has some difficulties, because denitration of secondary nitro compounds is a more difficult process than that of tertiary ones.[14] However, the secondary nitro groups, which are activated by a phenyl or carbonyl group, are readily replaced by hydrogen with Bu_3SnH under the same conditions as those of denitration of tertiary ones.[1] Thus, the Michael addition of phenylnitromethane followed by denitration with Bu_3SnH provides a new method for the conjugate addition of a benzyl group (eq 6).[15]



(9) Ono, N.; Kamimura, A.; Kaji, A. *Synthesis* **1984**, 226. The DBU–CH_3CN system is very effective for the Michael addition to less reactive olefins.

(10) The reaction of α,β-unsaturated nitriles with RCu BF_3 or R_2CuLi gives ketones as a main product.[2c] The reaction of α,β-unsaturated nitriles with $R_2Cu(CN)Li_2$ also fails to give the 1,4-addition products.[2e]

(11) Posner, G. H.; Tang, P. W. *J. Org. Chem.* **1978**, *43*, 4131.

(12) Additional activating groups are generally required for the facile conjugate addition of RMgX or R_2CuLi to α,β-unsaturated sulfoxides; see: Posner, G. H. "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983: Vol 2, pp 225–241.

(13) Liu, S. H. *J. Org. Chem.* **1977**, 42, 3209 and ref 2a.

(14) Ono, N.; Miyake, H.; Kaji, A. *J. Org. Chem.* **1984**, *49*, 4997.

Table I. Conjugate Addition of Secondary Alkyl Groups via Michael Addition of Nitroalkanes and Denitration[a]

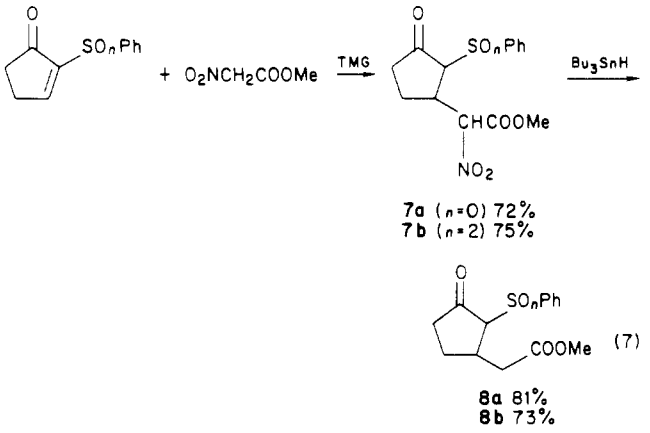
R^1		R^2	R^3	R^4	Y	base (equiv)	3, yield %	4, yield %
Me		n-C_6H_{13}	H	H	C(=O)Me	TMG (0.1)	**3a**, 80	**4a**, 82
	$-(CH_2)_4-$		H	H	C(=O)Me	TMG (0.1)	**3b**, 80	**4b**, 86
$PhCH_2$		Me	Ph	H	C(=O)Ph	DBU (1.0)	**3c**, 95	**4c**, 78
Me		Me_2CHCH_2	H	H	COOEt	TMG (0.1)	**3d**, 80	**4d**, 82
	$-(CH_2)_5-$		H	H	COOEt	TMG (0.1)	**3e**, 83	**4e**, 83
Me		Me	Ph	H	COOMe	DBU (1.0)	**3f**, 80	**4f**, 77
$PhCH_2$		Me	H	Me	COOMe	DBU (1.0)	**3g**, 90	**4g**, 77
Me		n-C_6H_{13}	H	H	CN	TMG (0.1)	**3h**, 82	**4h**, 85
	$-(CH_2)_4-$		H	H	CN	TMG (0.1)	**3i**, 84	**4i**, 90
$PhCH_2$		Me	Me	H	CN	DBU (1.0)	**3j**, 74	**4j**, 94
$PhCH_2$		Me	H	Me	CN	DBU (1.0)	**3k**, 95	**4k**, 87
Me		n-C_6H_{13}	H	H	CHO	Et_3N (0.1)	**3l**, 72	**4l**, 78
$PhCH_2$		Me	H	H	CHO	Et_3N (0.1)	**3m**, 77	**4m**, 65
Me		Me	H	H	SO_2Ph	TMG (0.1)	**3n**, 93	**4n**, 91
	$-(CH_2)_4-$		H	H	SO_2Ph	TMG (0.1)	**3o**, 90	**4o**, 85
Me		Me	Ph	H	SO_2Ph	DBU (1.0)	**3p**, 90	**4p**, 80
Me		Me	H	H	SOPh	DBU (1.0)	**3q**, 95	**4q**, 93
$PhCH_2$		Me	H	H	SOPh	DBU (1.0)	**3r**, 98	**4r**, 94

[a] Yields refer to pure isolated products. TMG = Tetramethylguanidine; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. The Michael addition was carried out at room temperature.

Table II. Conjugate Addition of Primary Alkyl Groups (eq 8)

R^1	R^2	Y	base (equiv)	9, % yield	10, % yield
$PhCH_2$	Me	COOMe	DBU (1)	**9a**, 85	**10a**, 53
Et	Ph	C(=O)Ph	DBU (1)	**9b**, 77	**10b**, 57
$PhCH_2$	Me	CN	DBU (1)	**9c**, 75	**10c**, 49
Et	Ph	SO_2Ph	DBU (1)	**9d**, 88	**10d**, 61
H	Ph	C(=O)Ph	TMG (1)	**9e**, 82	**10e**, 0

The Michael addition of methyl nitroacetate followed by denitration provides a new method for the conjugate addition of methyl acetate. Typical examples are presented in eq 7. Functional selectivity of the denitration

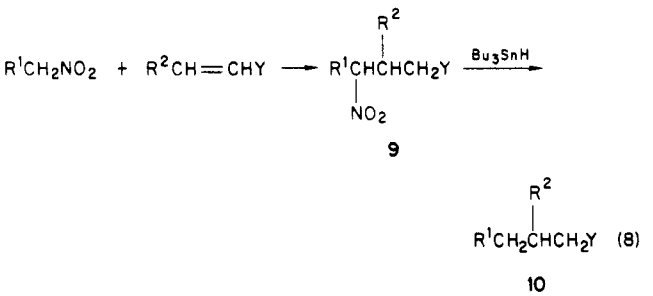


in eq 7 is remarkable in which the sulfur groups are not affected, while these groups are readily desulfurizated with Bu_3SnH if the nitro group is absent in the molecule.[16] Other secondary nitro groups which were not activated by special groups were not denitrated in good yields by this procedure. For example, heating a mixture of **9a**, which was prepared by the Michael addition of 1-nitro-2-phenylethane with methyl crotonate, Bu_3SnH (1.3 equiv), and AIBN (0.2 equiv) in benzene at 80 °C for 2 h gave **10a** in 12% yield, and unidentified products were mainly obtained. The yield of **10a** was somewhat improved by using

Table III. Conjugate Addition of 1-Cycloalkenylmethyl Groups (eq 9)

n	Y	11, % yield	12 + 13, % yield (12/13)
2	C(=O)Me	**11a**, 59	**12a**, **13a** 60 (53/47)
2	COOEt	**11b**, 58	**12b**, **13b** 62 (59/41)
2	CN	**11c**, 63	**12c**, **13c** 50 (52/48)
3	C(=O)Me	**11d**, 65	**12d**, **13d** 51 (68/32)
4	COOMe	**11e**, 60	**12e**, **13e** 58 (47/53)

Bu_3SnH in large excess. Heating a mixture of **9a**, Bu_3SnH (5 equiv), and AIBN (0.8 equiv) in toluene at 110 °C for 30 min gave **10a** in 53% yield. Thus, various primary alkyl groups can be introduced into electron deficient olefins. The results are summarized in Table II. The nitromethyl group is exceptional, there are no good methods for converting it to methyl group.



Conjugate Addition of Allyl Groups. The sequence of the Michael addition of allylic nitro compounds and the denitration provides a useful method for conjugate addition of allyl groups. Cyclic allylic nitro compounds are readily prepared by the reaction of cyclic ketones with nitromethane in the presence of bases.[17] The Michael addition of cyclic allylic nitro compounds with electron deficient olefins was carried out by using TMG as a catalyst to give the adduct, **11**, in about 60% yield. The subsequent treatment of **11** with Bu_3SnH gave a mixture of **12** and **13**. The latter compound was readily isomerized to **12** on treatment with acid. The results are summarized in Table III.

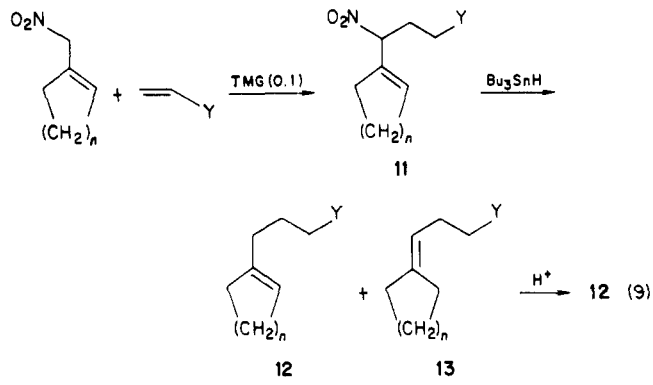
Acyclic allylic nitro compounds are also readily prepared by various methods.[18] α-Nitro olefins can be used directly

(15) The reactions of a benzyl organometallic reagent are often encountered by side reactions such as ortho attack; see: Danishefsky, S.; Migdalof, B. M. *J. Chem. Soc., Chem. Commun.* **1969**, 1107 and references therein.

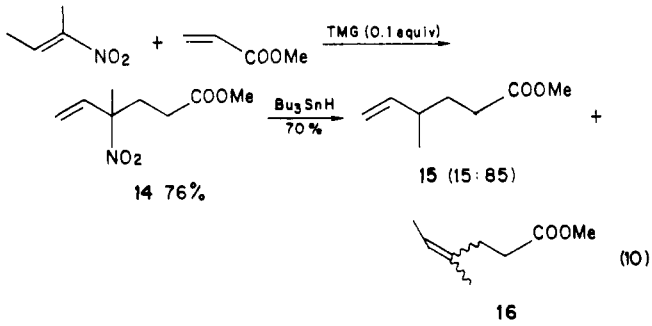
(16) (a) Ueno, Y.; Miyano, T.; Okawara, M. *Tetrahedron Lett.* **1982**, *23*, 443. (b) Gutierrez, C. G.; Summerhays, L. R. *J. Org. Chem.* **1984**, *49*, 5206.

(17) Houben-Weyl, "Methoden der Organischen Chemie", 4th ed.; Muller, E., Ed.; George Thieme Verlag: Stuttgart, 1971; Part I, Vol. X.

(18) Ono, N.; Hamamoto, I.; Yanai, T.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1985**, 523.

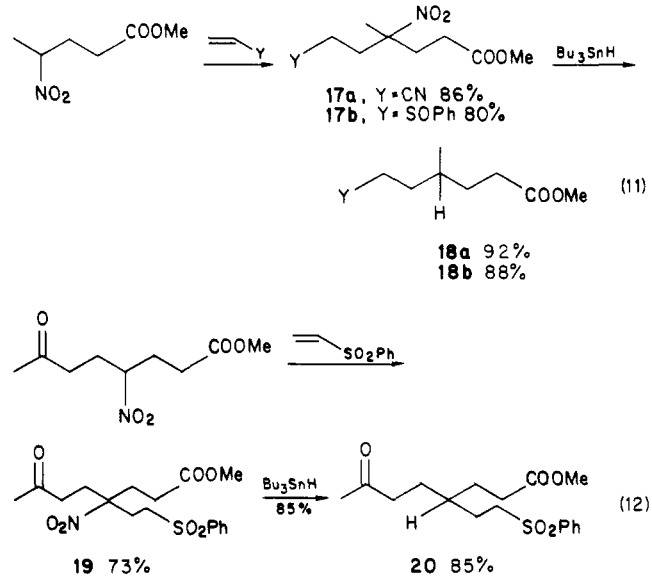


as allylic nitro compounds in the Michael addition, for α-nitro olefins are isomerized to allylic forms under basic conditions. For example, the reaction of 2-nitro-2-butene with methyl acrylate in the presence of TMG gave the Michael addition product, **14**, in 76% yield. Treatment of **14** with Bu_3SnH in the presence of AIBN at 80 °C gave a mixture of **15** and **16** with a ratio of 15:85.[19] Unfortunately it is very difficult to control the regiochemistry of denitration in this case.[20]

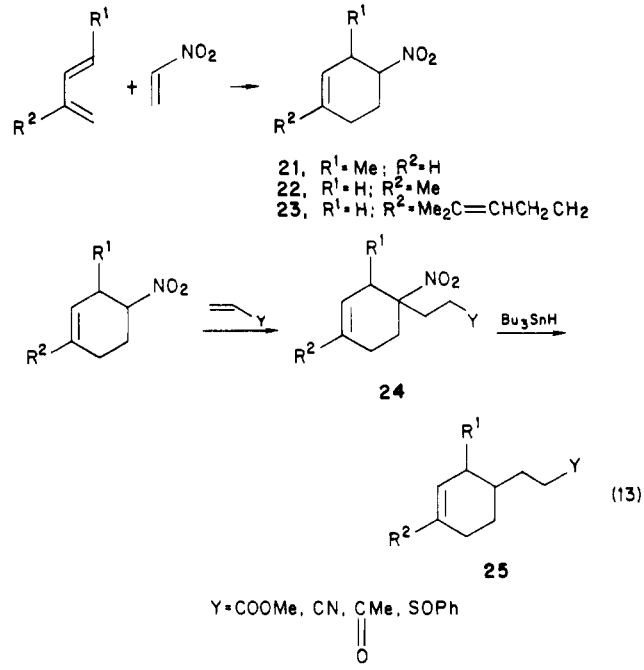


Conjugate Addition of Complex Alkyl Groups. Regiocontrolled conjugate addition of polyfunctionalized alkyl groups can be achieved by the present method. Typical examples are shown in eq 11 and 12. The Michael addition was carried out under the usual conditions and denitration was done by heating a mixture of the adduct, Bu_3SnH, and AIBN in benzene at 80 °C. Thus, polyfunctionalized compounds **18**, **19**, and **20** were prepared selectively without the use of protecting technique. Regiochemistry of the carbon–carbon bond formation and functional selectivity in the reaction of eq 11 and 12 are especially noteworthy.

As there are many methods to prepare aliphatic nitro compounds, various alkyl groups can be introduced to electron deficient olefins by this method. For example, the combination of the Diels–Alder reaction of α-nitro olefins, the Michael addition, and the denitration provides a useful method for the regioselective synthesis of cyclic compounds, where the nitro group enhances the reactivity and controls the direction of the Diels–Alder reaction.[21] The reaction of nitroethylene with 1,3-pentadiene, isoprene, or myrcene gave the adduct, **21**, **22**, or **23**, regioselectively in 79%, 86%, or 66% yield, respectively. The Michael addition of them to electron deficient olefins and



the denitration with Bu_3SnH gave **25**. The results are summarized in Table IV.



Thus, conjugate addition of rather complex alkyl groups can be done by very simple procedures and its regiochemistry is nicely controlled.

Conclusion

The results described in this paper have demonstrated the utility of denitro hydrogenation of aliphatic nitro compounds. Further, in view of regio- and stereoselective construction of the carbon frame work with properties of the nitro group, the present denitration with Bu_3SnH provides a new tool for organic synthesis.

Experimental Section

Materials. Nitro Compounds. Aliphatic nitro compounds were prepared by the reaction of alkyl bromides with sodium nitrite,[22] the reaction of aldehydes with nitroalkanes,[23] or the Michael addition of nitroethane to methyl acrylate.[24] 1-(Ni-

(19) It is noteworthy that treatment of allylic sulfones with Bu_3SnH gives allyl stannane via an S_H2' process; see: Ueno, Y.; Okawara, M. *J. Am. Chem. Soc.* **1979**, *101*, 1893.

(20) Recently, we have found that the nitro group of allylic nitro compounds is regioselectively denitrated by palladium-catalyzed reaction: see: Ono, N.; Hamamoto, I.; Kaji, A. "13th Symposium on Organometallic Chemistry"; Kyoto: Japan, 1983; Abstract p. 238.

(21) Ono, N.; Miyake, H.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1982**, 33.

(22) Kornblum, N. *Org. React.* **1962**, *12*, 101.

(23) Bachman, G. B.; Maleski, R. J. *J. Org. Chem.* **1972**, *37*, 2810.

Table IV. Conjugate Addition of 3-Cyclohexenyl Groups (eq 13)

R^1	R^2	Y	24, % yield	25, % yield
Me	H	COOMe	**24a**, 90	**25a**, 82
Me	H	CN	**24b**, 80	**25b**, 73
H	Me	CN	**24c**, 89	**25c**, 79
$Me_2C{=}CHCH_2CH_2$	H	COOMe	**24e**, 83	**25e**, 76
$Me_2C{=}CHCH_2CH_2$	H	SOPh	**24f**, 82	**25f**, 83

tromethyl)cycloalkenes were prepared by heating a solution of cycloalkanones, nitromethane, and piperidine (0.1 equiv) in benzene until the calculated amount of water was separated.[18] The Diels–Alder reaction of nitroethylene with 1,3-pentadiene, isoprene, or myrcene was carried out according to the literature.[25]

Michael Acceptor. Phenyl vinyl sulfoxide,[26] phenyl vinyl sulfone,[27] and 2-(phenylthio)-2-cyclopentenone[28] were prepared by the literature methods; other olefins are commercially available.

Conjugate Addition of Secondary Alkyl Groups. Preparation of 5-Methyl-2-undecanone (4a). Typical Procedure. To a solution of 2-nitrooctane (6.94 g, 43.6 mmol) and methyl vinyl ketone (2.77 g, 39.5 mmol) in 10 mL of acetonitrile was added tetramethylguanidine (TMG, 0.5 g, 4 mmol). The resulting solution was kept at room temperature for 24 h and the reaction mixture was poured into water (50 mL) containing 3 mL of 1 N HCl and extracted with ether. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was distilled to give 5-nitro-5-methyl-2-undecanone (**3a**): 7.2 g (80%); bp 124–127 °C (0.2 mmHg); IR (neat) 1160, 1390, 1530, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (t, J = 10 Hz, 3 H), 1.05–1.40 (m, 8 H), 1.46 (s, 3 H), 1.7–2.0 (m, 2 H), 2.0–2.2 (m, 2 H), 2.10 (s, 3 H), 2.2–2.5 (m, 2 H). A mixture of **3a** (0.89 g, 3.84 mmol), Bu_3SnH (1.47 g, 5.0 mmol), and AIBN (0.2 g) in 5 mL of benzene was heated at 80 °C for 2 h. Then the reaction mixture was subjected to column chromatography (silica gel/benzene–hexane) to give **4a**, 0.58 g (82%): IR (neat) 1160, 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.08–1.70 (m, 13 H), 2.05 (s, 3 H), 2.36 (t, J = 10 Hz, 2 H); MS, m/e (M^+) calcd for $C_{12}H_{24}O$ 184.1818, obsd 184.1817.

Preparation of 3,4-Dimethyl-5-phenylpentanenitrile (4j). The Michael addition of 2-nitro-1-phenylpropane to crotononitrile with DBU as a base was carried out in the same way as reported previously,[9] and 3,4-dimethyl-4-nitro-5-phenylpentanenitrile (**3j**) was obtained in 74% yield, mp 104–106 °C. A mixture of **3j** (0.61 g, 2.63 mmol), Bu_3SnH (0.99 g, 3.42 mmol), and AIBN (0.1 g) in 3 mL of benzene was heated at 80 °C for 2 h. The same workup as in the preparation of **4a** gave **4j**, 0.46 g (94%): IR (neat) 2250 cm^{-1}; NMR ($CDCl_3$) δ 0.78 (d, J = 8 Hz, 1.5 H), 0.80 (d, J = 8 Hz, 1.5 H), 0.99 (d, J = 10 Hz, 1.5 H), 1.05 (d, J = 10 Hz, 1.5 H), 1.6–2.0 (m, 2 H), 2.2 (m, 2 H), 2.6 (m, 2 H), 7.0–7.5 (m, 5 H); MS, m/e (M^+) calcd for $C_{13}H_{17}N$ 187.1360, obsd 187.1357.

Preparation of 4-Methyl-1-decanal (4l). A solution of 2-nitrooctane (1.59 g, 10 mmol), acrolein (1.0 g, 16 mmol), and triethlamine (0.1 g) in 5 mL of acetonitrile was kept at room temperature for 60 h. After the usual workup, distillation with Kugelrohr gave 4-methyl-4-nitro-1-decanal (**3l**): 1.50 g (72%); bp 180–200 °C (7 mmHg); IR (neat) 1380, 1540, 1700 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (t, J =v 8 Hz, 3 H), 1.05–1.40 (m, 8 H), 1.72 (s, 3 H), 1.8–2.6 (m, 6 H), 9.56 (s, 1 H). A mixture of **3l** (0.53 g, 20 mmol), Bu_3SnH (0.64 g, 22 mmol), and AIBN (0.1 g) in 5 mL of benzene was heated at 80 °C for 2 h. The usual workup gave **4l**: 0.27 g (78%); IR (neat) 1700 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (t, J = 4 Hz, 3 H), 1.24 (s, 3 H), 1.2–1.8 (m, 13 H), 2.44 (q, J = 10 Hz, 2 H), 9.60 (t, J = 4 Hz, 1 H); MS, m/e (M^+) calcd for $C_{11}H_{22}O$ 170.1699, obsd 170.1688. The following compounds, **4**, were prepared by these procedures.

4b:[29] IR (neat) 1160, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.9 (m, 11 H), 2.05 (s, 3 H), 2.36 (t, J = 8 Hz, 2 H); MS, m/e (M^+) calcd for $C_9H_{16}O$ 140.1201, obsd 140.1218.

4c: mp 75–83 °C; IR 1740 cm^{-1}; NMR ($CDCl_3$) δ 0.70 (d, J = 6 Hz, 1.5 H), 0.86 (d, J = 8 Hz, 1.5 H), 1.9–2.3 (m, 2H), 2.6–2.9 (m, 1 H), 3.3 (m, 3 H), 6.8–7.8 (m, 15 H). Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.36. Found: C, 87.88; H, 7.33.

4d: IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.83 (d, J = 6 Hz, 3 H), 0.85 (d, J = 6 Hz, 3 H), 1.19 (t, J = 7 Hz, 3 H), 1.3–1.9 (m, 5 H), 2.19 (t, J = 8 Hz, 2 H), 3.99 (q, J = 7 Hz, 2 H); MS, m/e (M^+) calcd for $C_{11}H_{22}O_2$ 186.1521, obsd 186.1519.

4e:[30] IR 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.24 (t, J = 8 Hz, 3 H), 1.1–2.0 (m, 13 H), 2.22 (t, J = 8 Hz, 2 H), 4.04 (q, J = 8 Hz, 2 H).

4f: IR 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.78 (d, J = 8 Hz, 3 H), 0.94 (d, J = 8 Hz, 3 H), 1.90 (m, 1 H), 2.4–3.0 (m, 3 H), 3.40 (s, 3 H), 7.5 (m, 5 H); MS, m/e (M^+) calcd for $C_{13}H_{18}O_2$ 206.1275, obsd 205.1272.

4g: IR 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.80 (d, J = 8 Hz, 1.5 H), 0.82 (d, J = 8 Hz, 1.5 H), 1.06 (d, J = 8 Hz, 1.5 H), 1.10 (d, J = 8 Hz, 1.5 H) 1.2–1.9 (m, 3 H), 2.2–2.8 (m, 3 H), 3.58 (s, 1.5 H), 6.9–7.2 (m, 5 H); MS, m/e (M^+) calcd for $C_{14}H_{20}O_2$ 220.1417, obsd 220.1412.

4h:[31] IR 2250 cm^{-1}; NMR $CDCl_3$) δ 0.90 (m, 6 H), 1.04–1.80 (m, 13 H), 2.29 (t, J = 8 Hz, 2 H).

4i: IR 2250 cm^{-1}; NMR ($CDCl_3$) δ 0.90–2.0 (m, 11 H), 2.32 (t, J = 10 Hz, 2 H); MS, m/e (M^+) calcd for $C_8H_{13}N$ 123.0966, obsd 123.0955.

4k: IR 2240 cm^{-1}; NMR ($CDCl_3$) δ 0.82 (d, J = 8 Hz, 3 H), 1.14 (d, J = 8 Hz, 3 H), 1.30–2.72 (m, 6 H), 6.9–7.3 (m, 5 H); MS, m/e (M^+) calcd for $C_{13}H_{17}N$ 187.1360, obsd 187.1377.

4m: IR 1705 cm^{-1}; NMR ($CDCl_3$) δ 0.80 (d, J = 8 Hz, 3 H), 1.18–1.80 (m, 3 H), 2.20–2.64 (m, 4 H), 6.9–7.3 (m, 5 H), 9.47 (s, 1 H); MS, m/e (M^+) calcd for $C_{12}H_{16}O$ 176.1190, obsd 176.1183.

4n: IR 1145, 1300 cm^{-1}; NMR ($CDCl_3$) δ 0.85 (d, J = 6 Hz, 6 H), 1.2–1.8 (m, 3 H), 3.0–3.3 (m, 2 H), 7.6 (m, 3 H), 7.8 (m, 2 H); MS, m/e (M^+) calcd for $C_{11}H_{16}SO_2$ 212.0931, obsd 212.0928.

4o: mp 60–62 °C; IR 1150, 1305 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.9 (m, 11 H), 3.0–3.2 (m, 2), 7.6 (m, 3 H), 7.8 (m, 2 H); MS, m/e (M^+) calcd for $C_{13}H_{18}SO_2$ 238.1027, obsd 238.1025.

4p: mp 97.5–98.5 °C; IR 1130, 1295 cm^{-1}; NMR ($CDCl_3$) δ 0.69 (d, J = 6 Hz, 3 H), 0.87 (d, J = 6 Hz, 3 H), 1.83 (m, 1 H), 3.00 (q, J = 6 Hz, 1 H), 3.55 (d, J = 8 Hz, 1 H), 6.8–7.6 (m, 10 H). Anal. Calcd for $C_{17}H_{20}SO_2$: C, 70.80; H, 6.99; S, 11.12. Found: C, 70.69; H, 6.86; S, 11.08.

4q: IR 1040 cm^{-1}; NMR ($CDCl_3$) δ 0.92 (d, J = 8 Hz, 6 H), 1.6 (m, 3 H), 2.80 (t, J = 10 Hz, 2 H), 7.5 (m, 5 H). This compound was further confirmed by the conversion to the sulfone, **4n**, with *m*-chloroperbenzoic acid.

4r: IR 1050 cm^{-1}; NMR ($CDCl_3$) δ 0.80 (d, J = 8 Hz, 1.5 H), 0.84 (d, J = 8 Hz, 1.5 H), 1.2–2.0 (m, 3 H), 2.3–2.6 (m, 2 H), 2.6–2.9 (m, 2 H), 7.0–7.4 (m, 5 H), 7.5 (m, 5 H). This was converted into the sulfone: mp 41.5–42 °C. Anal. Calcd for $C_{17}H_{20}SO_2$: C, 70.80; H, 6.99. Found: C, 70.86; H, 7.04.

Preparation of 5-Phenyl-2-pentanone (6a).[32] To a solution of phenylnitromethane (1.64 g, 12 mmol) and methyl vinyl ketone (0.70 g, 10 mmol) in 5 mL of acetonitrile was added diisopropylamine (0.1 g) and the resulting solution was kept at room temperature for 20 h. After the usual workup, distillation gave 5-nitro-5-phenyl-2-pentanone (**5a**), 1.74 g (84%). A mixture of **5a** (0.50 g, 2.42 mmol), Bu_3SnH (0.86 g, 2.95 mmol), and AIBN (0.1 g) in 5 ML of benzene was heated at 80 °C for 2 h. The same workup as in the preparation of **4a** gave **6a**: 0.31 g (79%)% IR (neat) 1160, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.80 (m, 2 H), 2.0 (s, 3 H), 2.35 (t, J = 8 Hz, 2 H), 2.55 (t, J = 8 Hz, 2 H), 7.0–7.3 (m, 5 H); MS, m/e (M^+) calcd for $C_{11}H_{14}O$ 162.1043, obsd 162.1040.

Methyl 4-Phenylbutyrate (6b):[15] IR 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.90 (m, 2 H), 2.20 (t, J = 10 Hz, 2 H), 2.60 (t, J = 10 Hz, 2 H), 3.58 (s, 3 H), 7.1 (m, 5 H).

Preparation of 2-(Phenylthio)-3-[(methoxycarbonyl)-

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methyl]cyclopentanone (8a). To a solution of 2-(phenylthio)-2-cyclopentenone (2.5 g, 13 mmol) and methyl nitroacetate (1.7 g, 15 mmol) in 30 mL of acetonitrile was added TMG (0.2 g). The resulting solution was kept at room temperature for 24 h. The usual workup followed by column chromatography (silica gel/benzene–hexane) gave **7a**: 2.7 g (72%); IR (neat) 1380, 1540, 1720, 1750 cm^{-1}; NMR ($CDCl_3$) δ 1.68–2.54 (m, 4 H), 2.78–3.08 (m, 1 H), 3.52 (d,d, J = 10 Hz, 1 H), 3.8 (t, J = 4 Hz, 3 H), 5.4–5.7 (m, 1 H), 7.2–7.6 (m, 5 H). Anal. Calcd for $C_{14}H_{15}NO_5S$: C, 54.36; H, 4.89; N, 4.53. Found: C, 54.39; H, 4.81; N, 4.48. A mixture of **7a** (0.74 g, 2.4 mmol), Bu_3SnH (0.78 g, 2.7 mmol), and AIBN (0.1 g) in 3 mL of benzene was heated at 80 °C for 2 h. Column chromatography (silica gel/benzene–hexane) gave **8a**: 0.52 g (81%); IR (neat) 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.4–3.2 (m, 8 H), 3.60 (s, 3 H), 7.1–7.5 (m, 5 H). Semicarbazone: mp 185–186 °C (lit.[25] mp 185–187 °C). The following compounds were prepared by these procedures.

7b: mp 88–89 °C; IR 1150, 1300, 1380, 1550, 1750 cm^{-1}; NMR ($CDCl_3$) δ 1.84–2.06 (m, 2 H), 2.38–2.66 (m, 3 H), 3.91 (s, 3 H), 4.19 (d, J = 7 Hz, 1 H), 5.7 (d, J = 5 Hz, 1 H), 7.5–7.9 (m, 5 H). Anal. Calcd for $C_{14}H_{15}NO_7S$: C, 49.36; H, 4.43; N, 4.10. Found: C, 49.33; H, 4.52; N, 4.12.

8b: IR 1150, 1310, 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.4–1.8 (m, 2 H), 2.2–3.4 (m, 5 H), 3.64 (s, 3 H), 3.84 (d, J = 10 Hz, 1 H), 7.6–7.9 (m, 5 H). Anal. Calcd for $C_{14}H_{16}O_5S$: C, 56.74; H, 5.44. Found: C, 56.88; H, 5.49.

Conjugate Addition of Primary Alkyl Groups. Preparation of Methyl 3-Methyl-5-phenylpentanoate (10a). A solution of 1-nitro-2-phenylethane (8.0 g, 53 mmol), methyl crotonate (4.0 g,40 mmol), and DBU (6.08 g,40 mmol) in 20 mL of acetonitrile was kept at room temperature for 22 h and the reaction mixture was poured into water and then acidified with dilute HCl. The usual workup followed by distillation gave methyl 3-methyl-4-nitro-5-phenylpentanoate (**9a**), 8.5 g (85%), bp 150–153 °C (1 mmHg). To a stirred solution of Bu_3SnH (2.94 g, 10.1 mmol), in 3 mL of toluene was added a solution of **9a** (0.50 g, 1.99 mmol) and AIBN (0.24 g) in 5 mL of toluene for 5 min at 110 °C and the resulting mixture was stirred at this temperature for an additional 25 min. The usual workup followed by column chromatography (silica gel/benzene–hexane) gave **10a**: 0.22 g (53%); IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.93 (d, J = 6 Hz, 3 H), 1.55 (q, J = 7 Hz, 2 H), 1.8–2.3 (m, 1 H), 2.11 (d, J = 8 Hz, 2 H), 3.53 (s, 3 H), 6.9–7.4 (m, 5 H); MS, m/e (M^+) calcd for $C_{13}H_{18}O_2$ 203.1306, obsd 206.1303. The following compounds were prepared by these procedures.

10b: mp 68–68.5 °C; IR 1670 cm^{-1}; NMR ($CDCl_3$) δ 0.83 (tm, J = 6 Hz, 3 H), 1.0–1.3 (m, 2 H), 1.5–1.8 (m, 2 H), 3.2 (m, 3 H), 7.1–7.9 (m, 10 H). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.89. Found: C, 85.74; H, 7.93.

10c: IR 2240 cm^{-1}; NMR ($CDCl_3$) δ 1.06 (d, J = 7 Hz, 3 H), 1.5–2.0 (m, 3 H), 2.20 (d, J = 6 Hz, 2 H), 2.88 (t, J = 7 Hz, 2 H), 7.0–7.4 (m, 5 H); MS, m/e (M^+) calcd for $C_{17}H_{15}N$ 173.1237, obsd 173.1242.

10d: mp 88.5–89.5 °C; IR 1130, 1300 cm^{-1}; NMR ($CDCl_3$) δ 0.83 (d, J = 7 Hz, 3 H), 1.0–1.3 (m, 2 H), 1.6–2.0 (m, 2 H), 3.1–3.4 (m, 1 H), 3.44 (m, 2 H), 6.9–7.8 (m, 10 H). Anal. Calcd for $C_{17}H_{20}SO_2$: C, 70.80; H, 6.98. Found: C, 70.55; H,6.78.

Conjugate Addition of Allyl Groups. Preparation of 5-(1-Cyclopentenyl)pentan-2-one (12a). To a solution of 1-(nitromethyl)cyclopentene (2.0 g, 15.7 mmol) and methyl vinyl ketone (0.91 g, 13 mmol) in 40 mL of acetonitrile was added a solution of TMG (0.1 g) in 10 mL of acetonitrile. The resulting solution was kept at room temperature for 15 h and worked up in the usual way. Distillation gave 5-(1-cyclopentenyl)-5-nitropentan-2-one (**11a**): 152 g (59%); bp 130–140 °C (1 mmHg). A mixture of **12a** (0.24 g, 1.2 mmol), Bu_3SnH (1.4 g, 4.8 mmol), and AIBN (0.16 g) in 10 mL of toluene was heated at reflux for 30 min and the reaction mixture was subjected to column chromatography (silica gel/benzene–hexane) to give a mixture of **12a** and **13a** whose ratio was determined by GLC and NMR to be 53:47: 0.11 g (60%); IR (neat) 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.6–2.04 (m, 6 H), 2.1–2.6 (m, 9 H), 5.1 (br s, exo =CH), 5.3 (br s, endo =CH). This mixture was heated with 6 N HCl in 3 Ml of EtOH at 80 °C for 8 h to give the pure **12a**: MS, m/e (M^+) calcd for $C_{10}H_{16}O$ 152.1164, obsd 152.1160. The following compounds were prepared by these procedures.

12b + 13b: IR 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 1.4–2.4 (m, 12 H), 4.0 (q, J = 7 Hz, 2 H), 5.1 (br s, exo =CH), 5.28 (br s, endo =CH); MS, m/e (M^+) calcd for $C_{11}H_{18}O_2$ 182.1303, obsd 182.1293.

12c + 13c: IR 2225 cm^{-1}; NMR ($CDCl_3$) δ 1.6–2.6 (m, 12 H), 6.18 (br t, exo =CH), 6.26 (br s, endo =CH); MS, m/e (M^+) calcd for $C_9H_{13}N$ 135.1017, obsd 135.1020.

12d + 13d: IR 1700 cm^{-1}; NMR ($CDCl_3$) β 1.4–1.8 (m, 6 H), 2.0 (s, 3 H), 1.8–2.2 (m, 4 H), 1.34 (t, J = 7 Hz, 2 H), 4.9 (m, exo =CH), 5.34 (br s, endo =CH); MS, m/e (M^+) calcd for $C_{11}H_{18}O$ 166.1358, obsd 166.1372.

12e + 13e: IR 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.9 (m, 8 H), 1.9–2.4 (m, 8 H), 3.60 (s, 3 H), 5.08 (br t, exo =CH), 5.52 (br t, endo =CH); MS, m/e (M^+) calcd for $C_{12}H_{20}O_2$ 196.1453, obsd 196.1452.

Denitration of Methyl 4-Methyl-4-nitro-5-hexanoate (14). A mixture of **14**[33] (0.28 g, 1.5 mmol), Bu_3SnH (0.48 g, 1.65 mmol), and AIBN (0.075 g) in 5 mL of benzene was heated at 80 °C for 1 h. Then the reaction mixture was subjected to column chromatography (silica gel/benzene/hexane) to give a mixture of **15** and **16**, 0.15 g (70%). The ratio of **15**:**16** was determined by GLC and NMR: IR 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.48–1.76 (m, Me of **15** and **16**), 2.12–2.54 (m, CH_2 of **15** and **16**), 3.56 (s, 3 He, 4.82–5.02 (m, CH_2=C of **15**), 5.04–5.28 (m, CH_2=C of **16**), 5.40–5.75 (m, CH=C of **15**).

Preparation of Methyl 6-Cyano-4-methylhexanoate (18a). A solution of methyl 4-nitropentanoate (1.6 g, 10 mmol), acrylonitrile (0.58 g, 11 mmol), and TMG (0.1 g) in 10 mL of acetonitrile was kept at room temperature for 24 h. The usual workup followed by distillation with Kugelrohr gave methyl 6-cyano-4-methyl-4-nitrohexanoate (**17a**): 1.85 g (86%); bp 190–200 °C (1 mmHg); IR (neat) 1535, 1720, 2250 cm^{-1}; NMR ($CDCl_3$) δ 1.62 (s, 3 H), 2.0–2.7 (m, 8 H), 3.68 (s, 3 H). A mixture of **17a** (1.07 g, 5.0 mmol), Bu_3SnH (1.75 g, 6.0 mmol), and AIBN (0.16 g, 1.0 mmol) in 5 mL of benzene was heated at 80 °C for 1.5 h. The reaction mixture was then subjected to column chromatography (silica gel/benzene–hexane) to give **18a**: 0.78 g (92%); IR (neat) 1730, 2250 cm^{-1}; NMR ($CDCl_3$) δ 0.96 (d, J = 8 Hz, 3 H), 1.1–1.9 (m, 5 H), 2.2–2.4 (m, 4 H), 3.59 (s, 3 H); MS, m/e (M^+) calcd for $C_9H_{15}NO_2$ 169.1102, obsd 169.1114. The following compounds were prepated by these procedures.

18b: DBU (1 equiv) was used at the step of the Michel addition; IR 1050, 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (m, 2 H), 1.2–1.8 (m, 5 H), 2.25 (t, J = 7 Hz, 2 H), 2.8 (m, 2 H), 3.60 (s, 3 H), 7.5 (m, 5 H); MS, m/e (M^+) calcd for $C_{14}H_{20}SO_3$ 268.1132, obsd 268.1121.

19: mp 96–97 °C; IR 1300, 1370, 1540, 1720 cm^{-1}; NMR ($CDCl_3$) δ 2.0–2.5 (m, 13 H), 3.0–3.3 (m, 2 H), 3.64 (s, 3 H), 7.5–8.0 (m, 5 H). Anal. Calcd for $C_{17}H_{23}NSO_7$: C, 52.98; H, 6.01; N, 3.63. Found: C, 52.76; H, 6.18; N, 3.80.

20: IR 1300, 1720, 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.8 (m, 7 H), 2.09 (s, 3 H), 2.1–2.5 (m, 4 H), 3.0–3.2 (m, 2 H), 3.6 (s, 3 H), 7.4–8.0 (m, 5 H). Anal. Calcd for $C_{17}H_{24}SO_5$: C, 59.98; H, 7.10. Found: C, 59.87; H, 7.14.

Conjugate Addition of 3-Cyclohexenyl Groups. Preparation of Methyl 3-(2-Methyl-3-cyclohexenyl)propanoate (25a). To a solution of 3-methyl-4-nitrocyclohexene (**21**, 1.03 g, m.3 mmol) and methyl acrylate (0.75 g, 8.8 mmol) in 10 mL of acetonitrile was added a solution of TMG (0.05 g) in 1 mL of acetonitrile and the resulting solution was kept at room temperature for 24 h. The usual workup followed by distillation with Kugelrohr gave 3-(2-methyl-1-nitro-3-cyclohexenyl)propanoate (**24a**), 1.45 g (90%), bp 180 °C (1 mmHg). A mixture of **24a** (0.58 g, 2.56 mmol), Bu_3SnH (0.82 g, 2.80 mmol), and AIBN (0.05 g) in 5 mL of benzene was heated at 80 °C for 2 h. The reaction mixture was then subjected to column chromatography (silica gel/benzene–hexane) to give **25a**: 0.38 g (82%); IR 1737 cm^{-1}; NMR ($CDCl_3$) δ 0.84, 1.00 (two d, J = 8 Hz, 3 H), 1.0–2.4 (m, 10 H), 3.60 (s, 3 H), 5.2–5.7 (m, 2 H); MS, m/e (M^+) calcd for $C_{11}H_{18}O_2$ 182.1306, obsd 182.1302. The following compounds were prepared by these procedures.

25b: IR 1650, 2250 cm^{-1}; NMR ($CDCl_3$) δ 0.86, 1.02 (two d, J = 8 Hz, 2 H), 1.1–2.6 (m, 10 H), 5.20–5.58 (m, 2 H); MS, m/e (M^+)

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calcd for $C_{10}H_{15}N$ 149.1203, obsd 149.1199.

25c: IR 1670, 2250 cm^{-1}; NMR ($CDCl_3$) δ 1.62 (s, 3 H), 1.0–2.2 (m, 9 H), 2.24–2.46 (m, 2 H), 5.16–5.34 (m, 1 H). Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.18; H, 10.21; N, 9.38.

25d: IR 1715 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (s, 3 H), 1.04–2.26 (m, 9 H), 2.06 (s, 3 H), 2.36 (t, J = 7 Hz, 2 H), 5.12–5.28 (m, 1 H). (2,4-Dinitrophenyl)hydrazone: mp 73–75 °C. Anal. Calcd for $C_{17}H_{22}N_4O_4$: C, 58.95; H, 6.40; N, 16.19. Found: C, 58.85; H, 6.21; N, 16.06.

25e: IR 1670, 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.56 (s, 3 H), 1.64 (s, 3 H), 0.92–2.16 (m, 13 H), 2.26 (t, J = 7 Hz, 2 H), 3.53 (s, 3 H), 4.84–5.06 (m, 1 H), 5.16–5.30 (m, 1 H). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.43.

25f: IR 1050 cm^{-1}; NMR ($CDCl_3$) δ 1.58 (s, 3 H), 1.64 (s, 3 H), 1.4–2.3 (m, 13 H), 2.8 (t, J = 8 Hz, 2 H), 5.0–5.2 (m,] H), 5.2–5.4 (m, 1 H), 7.4–7.8 (m, 5 H); MS, m/e (M^+) calcd for $C_{20}H_{28}SO$ 316.1859, obsd 316.1873.

Registry No. **1** (R^1 = Me, R^2 = n-C_6H_{13}), 4609-91-0; **1** (R^1R^2 = $(CH_2)_4$), 2562-38-1; **1** (R^1 = $PhCH_2$, R^2 = Me), 17322-34-8; **1** (R^1 = Me, R^2 = Me_2CHCH_2), 66553-37-5; **1** (R^1R^2 = $(CH_2)_5$), 1122-60-7; **1** (R^1 = R^2 = Me), 79-46-9; **1** (R^1 = $PhCH_2$, R^2 = H), 6125-24-2; **1** (R^1 = Et, R^2 = H), 108-03-2; **1** (R^1 = R^2 = H), 75-52-5; **1** (R^1 = Ph, R^2 = H), 622-42-4; **1** (R^1 = CH_2COOMe, R^2 = H), 2483-57-0; **2** (R^3 = R^4 = H, Y = COME), 78-94-4; **2** (R^3 = Ph, R^4 = H, Y = COPh), 94-41-7; **2** (R^3 = R^4 = H, Y = COOEt), 140-88-5; **2** (R^3 = Ph, R^4 = H, Y = COOMe), 103-26-4; **2** (R^3 = H, R^4 = Me, Y = COOMe), 80-62-6; **2** (R^3 = R^4 = H, Y = CN), 107-13-1; **2** (R^3 = Me, R^4 = H, Y = CN), 4786-20-3; **2** (R^3 = H, R^4 = Me, Y = CN), 126-98-7; **2** (R^3 = R^4 = H, Y = CHO), 107-02-8; **2** (R^3 = R^4 = H, Y = SO_2Ph), 5535-48-8; **2** (R^3 = Ph, R^4 = H, Y = SO_2Ph), 5418-11-1; **2** (R^3 = R^4 = H, Y = S(O)Ph), 20451-53-0; **2** (R^3 = Me, R^4 = H, Y = COOMe), 18707-60-3; **2** (R^3 = R^4 = H, Y = COOMe), 96-33-3; **2** (R^3 = R^4 = H, Y = NO_2), 3638-64-0; **3a**, 2562-42-7; **3b**, 97763-86-5; **3c**, 89706-88-7; **3d**, 97763-87-6; **3e**, 5498-73-7; **3f**, 75919-28-7; **3g**, 89706-86-5; **3h**, 97763-88-7; **3i**, 97763-89-8; **3j**, 91152-56-6; **3k**, 97763-90-1; **3l**, 82981-43-9; **3m**, 97763-91-2; **3n**, 58921-79-2; **3o**, 97763-92-3; **3p**, 91152-57-7; **3q**, 61174-01-4; **3r**, 83565-90-6; **4a**, 18216-72-3; **4b**, 18216-75-6; **4c**, 97763-93-4; **4d**, 97763-94-5; **4e**, 10094-36-7; **4f**, 97763-95-6; **4g**, 97763-96-7; **4h**, 97763-97-8; **4i**, 1123-04-2; **4j**, 97763-98-9; **4k**, 97763-99-0; **4l**, 80699-63-4; **4m**, 57919-02-5; **4n**, 52075-20-4; **4o**, 97764-00-6; **4p**, 97764-01-7; **4q**, 1918-88-3; **4r**, 83565-92-8; **5a**, 89861-56-3; **6a**, 2235-83-8; **6b**, 2046-17-5; **7a**, 78695-40-6; **7b**, 97764-24-4; **8a**, 62067-32-7; **8a** (semicarbazone), 62067-33-8; **8b**, 97764-25-5; **9a**, 89706-87-6; **9b**, 80460-05-5; **9c**, 97764-02-8; **9d**, 97764-03-9; **9e**, 6277-67-4; **10a**, 14983-20-1; **10b**, 1454-59-7; **10c**, 54089-83-7; **10d**, 97764-04-0; **11a**, 97764-05-1; **11b**, 97764-06-2; **11c**, 97764-07-3; **11d**, 97764-08-4; **11e**, 97764-09-5; **12a**, 55267-97-5; **12b**, 66050-54-2; **12c**, 97764-10-8; **12d**, 80376-43-8; **12e**, 97764-11-9; **13a**, 97764-12-0; **13b**, 97764-13-1; **13c**, 5732-70-7; **13d**, 20592-04-5; **13e**, 97764-14-2; **14**, 81769-17-7; **15**, 90112-90-6; **16**, 97764-27-7; **17a**, 97764-29-9; **17b**, 83565-97-3; **18a**, 97764-28-8; **18b**, 83566-00-1; **19**, 97764-30-2; **20**, 97764-31-3; **21**, 70391-76-3; **22**, 34969-96-5; **23**, 83566-01-2; **24a**, 97764-15-3; **24b**, 97764-16-4; **24c**, 97764-17-5; **24d**, 97764-18-6; **24e**, 97764-19-7; **24f**, 97764-33-5; **25a**, 90611-59-9; **25b**, 97764-20-0; **25c**, 97764-21-1; **25d**, 97764-22-2; **25d** (dinitrophenylhydrazone), 97764-34-6; **25e**, 97764-23-3; **25f**, 97764-32-4; TMG, 113-00-8; DBU, 31171-04-7; $MeCHNO_2(CH_2)_2COOMe$, 10312-37-5; $MeCO(CH_2)_2CHNO_2(CH_2)_2COOMe$, 61426-51-5; CH=CHCH=CHMe, 504-60-9; 2-(phenylthio)-2-cyclopentenone, 34780-08-0; 2-(phenylsulfonyl)-2-cyclopentenone, 97764-26-6; 1-(nitromethyl)-cyclopentene, 2562-42-7; 1-(nitromethyl)cyclohexene, 5330-61-0; 1-(nitromethyl)cycloheptene, 52315-51-2; isoprene, 78-79-5; myrcene, 123-35-3.

Stable Long-Chain Fluoroxy Compounds and Their Chemistry†

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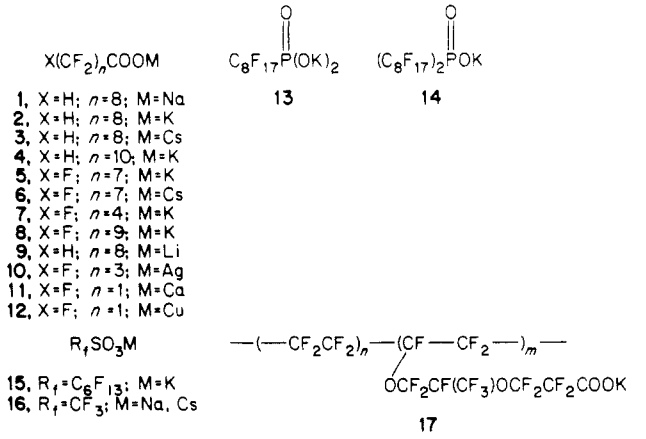
Certain alkalai metal salts of long-chain perfluorinated acids were reacted with nitrogen-diluted fluorine to produce oxidative solutions. The reaction conditions can be controlled to afford mainly acyl hypofluorites (R_fCOOF) or fluoroxy species [R_fCF_2OF and $R_fCF(OF)_2$] which have been identified by both chemical reactions and ^{19}F NMR studies. These solutions are useful in electrophilic fluorination reactions and as initiators for the polymerization of some fluorinated monomers. As initiators they produce polymers with fewer reactive end groups when compared with standard methods of initiation.

Introduction

The mild and selective introduction of fluorine into organic molecules continues to be of interest[1] because of potentially important applications to the areas of agrichemicals and pharmaceuticals.[2] A variety of electrophilic fluorinating agents including F_2,[3] CF_3OF,[4] CF_3CF_2OF,[5] XeF_2,[6] CF_3COOF,[7] and CH_3COOF[8] have been developed and utilized for this purpose. However, most of these materials are gaseous or highly volatile, some cannot be stored for long periods of time and ideally are prepared just prior to use, and some are too expensive for ordinary routine work. It was the objective of our program then to develop nonvolatile electrophilic fluorinating agents which could be conveniently handled and stored for long periods of time at least in solution. A possible answer to these problems seemed to lie in the preparation of the fluoroxy derivatives of long-chain perfluoroalkyl acids.

Chart I



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