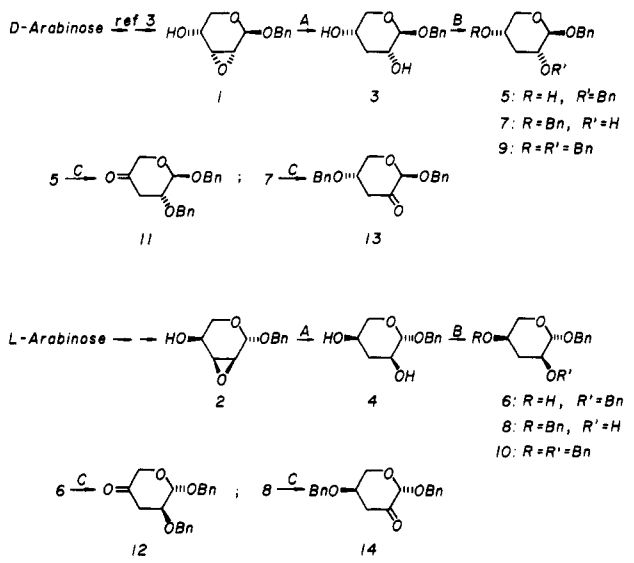
Table I. Yields and Physical Data for Compounds 1–14

product[a]	method	yield,[b] %	$[\alpha]^{20c}_D$, deg	mp, °C	R_f[d]	^{1}H NMR[e]	^{13}C NMR[f]
1	ref 3	58[g]	−63 (c 1.4)	76.5–78.0	0.27	5.04 (s)	93.5, 62.1, 61.6, 51.8
2		55[g]	+65 (c 1.1)	75.0–78.0	0.27	5.04 (s)	93.5, 62.1, 61.6, 51.8
3	A	68, 17[h]	−146 (c 1.9)	92.5–93.5	0.11	4.77 (s)	98.9, 66.9, 65.5, 64.7, 30.8
4	A	80, 16[h]	+144 (c 1.0)	92.5–94.0	0.11	4.77 (s)	98.9, 66.9, 65.5, 64.7, 30.8
5	B	33	−109 (c) 0.8)	oil	0.34	4.91 (d, J = 1.3 Hz)	96.0, 73.8, 65.1, 65.0, 28.6
6	B	38	+104 (c 1.2)	oil	0.34	4.91 (d, J = 1.3 Hz)	96.0, 73.8, 65.1, 65.0, 28.6
7	B	22	−119 (c 0.8)	49.0–50.0	0.54	4.78 (d, J = 2.2 Hz)	99.5, 72.2, 66.7, 60.8, 28.9
8	B	26	+118 (c 0.5)	48.0–50.0	0.54	4.72 (d, J = 2.2 Hz)	99.5, 72.2, 66.7, 60.8, 28.9
9	B	19	−35 (c 0.7)	36.0–37.0	0.70	4.54 (s)	103.1, 74.5, 71.6, 66.4, 33.9
10	B	16	+25 (c 0.9)	36.0–37.0	0.70	4.54 (s)	103.1, 74.5, 71.6, 66.4, 33.9
11[i]	C	82	−110 (c 0.8)	oil	0.63	5.01 (d, J = 2.5 Hz)	206.3, 97.1, 75.2, 67.6, 40.5
12	C	81	+116 (c 0.6)	oil	0.63	5.01 (d, J = 2.5 Hz)	206.3, 97.1, 75.2, 67.6, 40.5
13	C	60	−138 (c 1.0)	78.5–79.5	0.61	4.79 (s)	200.2, 98.6, 75.3, 60.8, 40.8
14[i]	C	79	+142 (c 0.6)	78.5–79.5	0.61	4.79 (s)	200.2, 98.6, 75.3, 60.8, 40.8

[a] Satisfactory analytical data were reported for all new crystalline compounds listed in the table. [b] Isolated yield. [c] In chloroform. [d] SiO_2, ethyl acetate:hexane, 1:1. [e] $CDCl_3$, Me_4Si, ppm, anomeric proton signal. [f] $CDCl_3$, Me_4Si, ppm, sugar ring carbon signals. [g] Overall yield from D- and L-arabinose, respectively. [h] Starting material recovered in reaction B. [i] IR (cm^{-1}) 11, 1740; 14, 1750.

Scheme I[a]



[a] A, Red Al/THF; B, $NaH/PhCH_2Cl/DMF$; C, $(COCl)_2/Me_2SO/(i\text{-}Pr)_2NEt/CH_2Cl_2$.

hydroxyl group could influence the stereoselective delivery of hydride.

Benzylation of **3** and **4** with 1 equiv of benzyl chloride gave **5**, **7**, **9**, and **6**, **8**, **10**, respectively. These compounds were easily separated by column chromatography (see R_f values in Table I). Oxidation[6] of **5**, **6**, **7**, and **8** gave the ketones **11**, **12**, **13**, and **14**, respectively, which are suitable starting materials for the synthesis of enantiomerically pure compounds. This aspect is currently under investigation in our laboratory.

Experimental Section

Method A. The epoxy alcohol **2** (11.1 g; 50.0 mmol) was dissolved in tetrahydrofuran (300 mL) and the solution was cooled (0 °C). Sodium bis(2-methoxyethoxy)aluminum hydride (Red Al, 79% in toluene, 45 mL, 150 mmol) was added dropwise under nitrogen and the mixture was stirred overnight. Water (30 mL) was added dropwise with cooling. Extraction with ether, drying (Na_2SO_4), and concentration gave **4** (11.2 g, 100%). Recrystallization from ethyl acetate:hexane gave pure **4** (8.97 g, 80%).

Method B. Sodium hydride (1.88 g, 37.5 mmol) was dissolved in dimethylformamide (175 mL) and the diol **4** (8.40 g, 37.5 mmol) was added. After 3 h, benzyl chloride (4.76 g, 37.5 mmol) was added dropwise (50–60 °C) and the mixture was stirred overnight and finally partitioned between dichloromethane and water. The organic phase was dried ($MgSO_4$), co-distilled with toluene, and subjected to chromatography (SiO_2, ethyl acetate:hexane, gradient 1:10 → 1:5 → 1:2 → ethyl acetate) to give **6**, **8**, **10**, and recovered **4** (see Table I).

Method C. Dimethyl sulfoxide (1.40 g, 17.9 mmol) in dichloromethane (10 mL) was added to a cooled (−60 °C) solution of oxalyl chloride (1.14 g, 8.98 mmol) in dichloromethane (15 mL). After 10 min, alcohol **8** (2.36 g, 7.52 mmol) in dichloromethane (10 mL) was added, followed by diisopropylethylamine (3.50 g, 37.6 mmol) after further 15 min. When the mixture had reached room temperature, water (20 mL) was added and the organic phase was washed with water, dried ($MgSO_4$), and concentrated to give crystalline **14** (in analogous preparations, **11** and **12** were isolated by column chromatography: SiO_2, ethyl acetate:hexane, 1:10).

Acknowledgment. This work was supported by the Swedish Natural Science Research Council and the Swedish Board for Technical Development.

Registry No. 1, 67412-71-9; 2, 65359-87-7; 3, 56809-43-9; 4, 91632-08-5; 5, 91632-09-6; 6, 91632-10-9; 7, 91632-11-0; 8, 91632-12-1; 9, 91632-13-2; 10, 91632-14-3; 11, 91632-15-4; 12, 91632-16-5; 13, 91632-17-6; 14, 91632-18-7.

(6) Omura, K.; Swern, D. *Tetrahedron* 1978, *34*, 1651.

Perfluoroalkyl Isocyanates: General Synthesis by the Pyrolysis of Disilyl Esters of Hydroxamic Acids†

William J. Middleton

Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Received November 22, 1983

Trifluoromethyl isocyanate and other perfluoroalkyl isocyanates are usually prepared by the classical Curtius Rearrangement,[1] since routes based on the phosgenation of the unstable α-fluoroamines are not possible. However, the acyl azide precursors needed are capriciously explosive, and at least two investigators have been injured while trying to prepared trifluoromethyl isocyanate by this method. Recent work by us has demonstrated that 2-(trifluoromethyl)-1,3,4-dioxazol-2-one is another efficient intermediate to trifluoromethyl isocyanate, but this intermediate is also capriciously explosive.[2]

We now report a general, high yield method for preparing perfluoroalkyl isocyanates that is both safe and convenient. A modification of the Lossen rearrangement,[3]

† Contribution No. 3307.

0022-3263/84/1949-4541$01.50/0

Table I. Trimethylsilyl *N*-Trimethylsiloxy Imidates

$R_fC(OSi(CH_3)_3)=NOSi(CH_3)_3$ and $(CH_3)_3SiON=CR_fC(OSi(CH_3)_3)=NOSi(CH_3)_3$

R_f	formula	bp, °C (mm)	yield, %	Anal.[a]	IR (C=N), cm^{-1}	^{19}F NMR ($CDCl_3$), ppm
CH_2F	$C_8H_{20}FNO_2Si$	66.4 (6)	72	C, H, N	1640	−225.6 (t, J = 47.5 Hz) 12% Z isomer −237.4 (t, J = 47.5 Hz) 88% E isomer
CHF_2	$C_8H_{19}F_2NO_2Si_2$	53.6 (9)	57	C, H	1650	−123.1 (d, J = 54 Hz)
CF_3	$C_8H_{18}F_3NO_2Si_2$[b]	48 (10)	80	C, H, F, N	1655	−73.5 (s)
CF_3CF_2	$C_9H_{18}F_5NO_2Si_2$	43 (5)	72	C, H, F, N	1655	−83.1 (3 F), −119.9 (2 F)
$CF_3CF_2CF_2$	$C_{10}H_{18}F_7NO_2Si_2$	51 (3.5)	74	C, H, F, N	1655	−81.2 (3 F), −117.7 (2 F), −126.9 (2 F)
$CF_3(CF_2)_6$	$C_{14}H_{18}F_{15}NO_2Si_2$	74 (0.3)	98	C, H, F, N	1655	−81.5 (3 F), −116.7 (2 F), −122.2 (2 F), −122.4 (4 F), −122.7 (2 F), −126.7 (2 F)
$CF_2CF_2CF_2$	$C_{17}H_{36}F_6N_2O_4Si_4$	113.2 (0.5)	42	C, H, N	1650	−116.6 (4 F), −122.5 (2 F)
CF_2	$C_{15}H_{36}F_2N_2O_4Si_4$	104 (0.5)	96	C, H, F, N	1655	−109.3 (s)

[a] Analyses indicated were within 0.4% of the theoretical value. [b] Lidy, W.; Sundermeyer, W. *Chem. Ber.* **1976**, 2542.

Table II. Fluorine-Containing Isocyanates

isocyanate	formula	bp, °C	yield, %	Anal.[a]	^{19}F NMR ($CDCl_3$), ppm
CH_2FNCO[b]	C_2H_2FNO	41.7–41.8	69	C, H, F[c]	−168.3 (t, J = 49 Hz)
CHF_2NCO[b]	C_2HF_2NO	12.6	59		−81.3 (d, J = 68 Hz)
CF_3NCO	C_2F_3NO	−20.4	85		−45.8 ($^1/_2w$ = 6 Hz)
CF_3CF_2NCO	C_3F_5NO	−10	66		−85.4 (2 F), 87.5 (3 F)
$CF_3CF_2CF_2NCO$	C_4F_7NO	24–26	83	C, F, N	−81.1 (2 F), 81.4 (3 F), −128.4 (2 F)
$CF_3(CF_2)_6NCO$	$C_8F_{15}NO$	121–122	55	C, F, N	−80.0 (2 F), −81.6 (3 F), −122.0 (4 F), −122.9 (2 F), −123.7 (2 F), −126.5 (2 F)
$CF_2(CF_2NCO)_2$	$C_5F_6N_2O_2$	64–65	75	C, F, N	−79.7 (4 F), −125.8 (2 F)
$CF_2(NCO)_2$	$C_3F_2N_2O$	40–41	65	C, F, N	−34.6 (s)

[a] Analyses indicated were within 0.4% of the theoretical value. [b] Previously reported but not characterized: Hückel, W. *Nachr. Akad. Wiss. Gottingen, Math.-physik.Klasse* **1946**, 36. [c] Analysis of polymer.

which consists of the pyrolysis of disilyl esters of perfluorohydroxamic acids **2** at 250–300 °C, gives good yields of the isocyanates **4** along with the chemically inert byproduct hexamethyldisiloxane (**5**). Neither the starting materials, intermediates, nor byproducts appear to be explosive.

$$\underset{\mathbf{1}}{R_fC(=O)NHOH} \xrightarrow{HMDS} \underset{\mathbf{2}}{R_fC(OSi(CH_3)_3)=NOSi(CH_3)_3} \xrightarrow{\Delta} \underset{\mathbf{3}}{[R_fC(=O)N:]} \longrightarrow R_fN=C=O + (CH_3)_3Si)_2O$$

This synthesis is general for the preparation of a variety of perfluoro and partially fluorinated isocyanates, as demonstrated by the preparation of fluoromethyl, difluoromethyl, trifluoromethyl, pentafluoroethyl, heptafluoropropyl, and perfluoroheptyl isocyanates. Difunctional isocyanates were also prepared, including hexafluoro-1,3-propylene diisocyanate and the previously unknown difluoromethylene isocyanate (**6**).

$$CF_2(CO_2CH_3)_2 \xrightarrow{NH_2OH} \underset{\mathbf{7}}{CF_2(CONHOH)_2} \xrightarrow{HMDS}$$

$$(CH_3)_3SiON=C(OSi(CH_3)_3)CF_2C(OSi(CH_3)_3)=NOSiCH_3)_3 \xrightarrow{\Delta} \underset{\mathbf{6}}{CF_2(NCO)_2} + \mathbf{5}$$

The disilyl starting materials were prepared by treating the hydroxamic acids with hexamethyldisilazane (HMDS) in acetonitrile at 25 °C. The hydroxamic acids were prepared by the room-temperature reaction of hydroxylamine in methanol with esters of the corresponding carboxylic acids. Thus, the overall synthesis starts with the readily available esters of perfluoro carboxylic acids and converts them safely to perfluoroalkyl isocyanates in good yield.

Experimental Section

Fluorine NMR spectra were obtained on a Varian XL-100 instrument operated at 94.1 MHz with $CFCl_3$ as an internal standard. Upfield shifts are reported as negative values.

Disilation of Hydroxamic Acids (Table I). Hexamethyldisilazane, 1.5 mol, was added dropwise to a solution of 0.5 mol of the hydroxamic acid (0.25 mol for the difunctional hydroxamic acids) in 150 mL of acetonitrile at ambient temperature. The reaction mixture was stirred for 18 h and then distilled through a spinning band column to give the disilyl derivatives as a colorless liquid. All derivatives listed in Table I showed similar proton NMR, typically ^1H NMR ($CDCl_3$) δ 0.17 (s, 9 H) and 0.21 (s, 9 H). Only the derivative prepared from fluoroacetohydroxamic acid showed the presence of both the E and Z isomers (four closely spaced lines in the proton NMR near Me_4Si).

Pyrolysis of Trimethylsilyl *N*-Trimethylsiloxy Imidates 2. Heptafluoropropyl isocyanate was prepared by adding dropwise 103.65 g (0.277 mol) of trimethylsilyl 2,2,3,3,4,4,4-heptafluoro-*N*-(trimethylsiloxy)butaneimidate through an unpacked $^1/_2$-in. stainless steel tube inclined at an angle of 30° and heated to 375 °C over a length of 12 in. The pyrolysate was condensed in a cold trap (−78 °C) and then distilled through a 12-in. spinning band column to give 48.75 g (83%) of heptafluoropropyl isocyanate as a colorless liquid, bp 24.5–24.7 °C; and 33.2 g (90%) of hexamethyldisiloxane, bp 99–100 °C. The other isocyanates listed in Table II were prepared similarly by pyrolysis of the corresponding disilyl compounds. Fluoromethyl isocyanate polymerized to a white solid after a few hours at ambient temperature.

Hydroxamic Acids. Trifluoroaceto-, pentafluoropropiono-, heptafluorobutyno-, and perfluorooctanohydroxamic acids were prepared as previously described.[2] Fluoroacetohydroxamic acid was prepared similarly from ethyl fluoroacetate in 82% yield and was obtained as colorless crystals: mp 92–94 °C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.92 (d, J = 45 Hz), 8.8 (br NH, OH); ^{19}F NMR ($CDCl_3$) δ −230.3 (t, J = 45 Hz). Difluoroacetohydroxamic acid was prepared similarly from ethyl difluoroacetate in 94% yield and was obtained as a colorless oil: n^{25}_D 1.4402; ^1H

(1) Barr, D. A.; Haszeldine, R. N. *J. Chem. Soc.* **1956** 3428. Sprenger, G. H.; Wright, K. J.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 2890.
(2) Middleton, W. J. *J. Org. Chem.* **1983**, *48*, 3845.
(3) Rigaudy, J.; Lytwyn, E.; Wallach, P.; Cuong, N. K. *Tetrahedron Lett.* **1980**, *21*, 3367.

NMR ($CDCl_3$) δ 6.1 (t, J = 54 Hz) and 9.7 (br NH, OH); ^{19}F NMR ($CDCl_3$) δ −126.3 (d, J = 54 Hz).

2,2-Difluoro-*N*,*N*′-dihydroxy-1,3-propanediamide (7). A solution of 1.19 mol of sodium methoxide in 500 mL of methanol was added dropwise to a stirred suspension of 82.71 g (1.19 mol) of hydroxylamine hydrochloride in 150 mL of methanol. The precipitated NaCl was filtered off, and 100 g (0.595 mol) of dimethyl difluoromalonate[4] was added dropwise. The reaction mixture was stirred overnight and then evaporated to dryness to give 100 g (99% yield) of 2,2-difluoro-*N*,*N*′-dihydroxy-1,3-propanediamide as colorless crystals. A sample was recrystallized from acetonitrile: mp 143–145 °C; IR (KBr) 1715 cm^{-1} (C=O); ^{19}F NMR (acetone-d_6) δ −114.6 (s). Anal. Calcd for $C_3H_4F_2N_2O_4$: C, 21.19; H, 2.37; F, 23.34; N, 16.47. Found: C, 20.89; H, 2.44; F, 22.28; N, 16.47.

2,2,3,3,4,4-Hexafluoro-*N*,*N*′-dihydroxy-1,5-pentanediamide. A solution of 0.168 mol of sodium methoxide in 100 mL of methanol was added dropwise to a stirred suspension of 11.8 g (0.168 mol) of hydroxylamine hydrochloride in 50 mL of methanol. The precipitate, NaCl, was filtered off, and 24.87 g (0.084 mol) of diethyl perfluoroglutarate was added to the filtrate. The reaction mixture was stirred overnight and then evaporated to dryness to give 22.0 g (97% yield) of 2,2,3,3,4,4-hexafluoro-*N*,*N*′-dihydroxy-1,5-pentanediamine as colorless crystals. A sample was recrystallized from ethyl acetate for analysis: mp 156–160 °C; IR (neat) 1680 cm^{-1} (C=O); ^{19}F NMR (Me_2SO-d_6) δ −118.6 (4 F), −122.9 (2 F). Anal. Calcd for $C_5H_4F_6N_2O_4$: C, 22.24; H, 1.49; N, 10.37. Found: C, 22.21; H, 1.68; N, 9.70.

Registry No. 1 (R_f = CH_2F), 760-29-2; 1 (R_f = CHF_2), 92144-81-5; 1 (R_f = CF_3), 1514-45-0; 1 (R_f = CF_3CF_2), 87051-00-1; 1 (R_f = $CF_3(CF_2)_2$), 87050-96-2; 1 (R_f = $CF_3(CF_2)_6$), 15435-88-8; (*Z*)-2 (R_f = CH_2F), 92144-84-8; (*E*)-2 (R_f = CH_2F), 92144-92-8; 2 (R_f = CHF_2), 92144-85-9; 2 (R_f = CF_3), 60556-44-7; 2 (R_f = CF_3CF_2), 92144-86-0; 2 (R_f = $CF_3(CF_2)_2$), 92144-87-1; 2 (R_f = $CF_3(CF_2)_6$), 92144-88-2; 4 (R_f = CH_2F), 462-48-6; 4 (R_f = CHF_2), 372-10-1; 4 (R_f = CF_3), 460-49-1; 4 (R_f = CF_3CF_2), 356-74-1; 4 (R_f = $CF_3(CF_2)_2$), 424-62-4; 4 (R_f = $CF_3(CF_2)_6$), 335-91-1; 6, 92144-91-7; 7, 92144-83-7; $Me_3SiNHSiMe_3$, 999-97-3; $HONHC(O)(CF_2)_3C(O)NHOH$, 92144-82-6; $Me_3SiOH{=}C(OSiMe_3)(CF_2)_3C(OSiMe_3){=}NOSiMe_3$, 92144-89-3; $Me_3SiON{=}C(OSiMe_3)CF_2C(OSiMe_3){=}NOSiMe_3$, 92144-90-6; $CF_2(CF_2NCO)_2$, 13044-43-4; $FCH_2C(O)OEt$, 459-72-3; $F_2CHC(O)OEt$, 454-31-9; $F_2C(C(O)OMe)_2$, 379-95-3; $EtOC(O)(CF_2)_3C(O)OEt$, 424-40-8.

(4) England, D. C.; Kraft, R. L.; Krespan, C. G. U.S. Patent 4 316 986, 1982.

Synthesis under High Pressure. Michael Additions to a Sterically Hindered Steroidal 4-En-3-one System[1,2]

Shiro Hashimoto, Kiyoshi Matsumoto,* and Shinichi Otani

Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received April 3, 1984

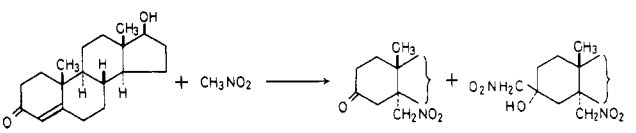
Michael additions to the C-1 and C-5 in steroidal 1-en-3-one and 4-en-3-one systems are generally difficult to achieve, probably due to steric hindrance; they are limited to attack of cyanide and/or phenyl thiolate ion.[3] Indeed, Michael additions of nitromethane[4] to these steroidal enones have been reported to be unsuccessful.[3c] The steroidal 4-en-3-one system is apparently more hindered than the 1-en-3-one system since sulfur nucleophiles are reported to give 1α adducts with 1,4-dien-3-one.[3c,5] Thus, in view of recent work on high pressure Michael reactions,[6,7] we chose to investigate the problem using testosterone (1) as a first example of 4-en-3-one systems.

Table I. Michael Addition of Testosterone (1) with Nitromethane (2) at 9 kbar and 30 °C for 6 Days

				isolated yield, %		
entry	1, mmol	2, mmol	catalyst/solvent	3	4	1
1[a]	5	50	0.5 M TBF/THF	8	5	81
2	5	50	0.5 M TBF/THF	5	79	5
3	5	10	0.5 M TBF/THF	22	36	18
4	5	5	0.5 M TBF/THF	25	15	41
5	3	30	DBU(3 mmol)/CH_3CN	4	57	8
6	3.5	7	DBU(3.5 mmol)/CH_3CN	38	7	31

[a] At 1 bar and room temperature for 1 week.

At atmospheric pressure, 1 is inert to nitromethane (2) in the presence of such bases as 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and triethylamine. The reaction of 1 with excess of 2 catalyzed by tetra-*n*-butylammonium fluoride (TBF)[8] proceeds poorly (ca. 10% after 1 week). At high pressure, the reaction of 1 with 2 was carried out either in 0.5 M TBF/THF or DBU/CH_3CN in a 8-mL Teflon capsule stored for 6 days at 900 MPa (1 MPa ≈ 10 atm) and ca. 30 °C. The usual workup and chromatographic separation (see Experimental Section) gave the 1:1 adduct 3, mp 209–211 °C and the 1:2 adduct 4, mp 172–174 °C.



1 2 3 4

The results are summarized in Table I. Both 3 and 4 appeared to be a single substance as revealed by ^{13}C NMR and TLC (Experimental Section). The configuration of these adducts is presumed to be 5α-nitromethyl and 3β,5α-bis(nitromethyl), respectively, based upon steric consideration. The use of a large excess of 2 led to the predominant formation of 4 arising from initial Michael addition followed by nitro-aldol reaction (entries 2 and 5). The formation of 4 could be considerably suppressed by employing 1 or 2 equiv of 2 (entries 3, 4, and 6), although this also led to lower conversion. For this purpose, DBU in acetonitrile proved to be a superior base.

Thus, the high pressure Michael addition may be useful for functionalization of the sterically hindered steroidal 4-en-3-one systems. Our studies on the high pressure Michael additions of other steroidal enones to a variety of nucleophiles are continuing.

(1) Dedicated to Professor N. H. Cromwell on the occasion of his retirement and of his 70th birthday.

(2) Presented at the 49th National Meeting of the Chemical Society of Japan, April, 1984, Tokyo.

(3) (a) Nagata, W.; Hirai, S.; Itazaki, H.; Takeda, K. *J. Org. Chem.* **1961**, *26*, 2413. (b) Nagata, W.; Yoshioka, M.; Murakami, M. *J. Am. Chem. Soc.* **1972**, *94*, 4654. (c) Campbell, M. M.; Jigajinni, V. R.; Wightman, R. H. *Tetrahedron Lett.* **1979**, 2455; *J. Chem. Res., Synop.* **1981**, 184; *J. Chem. Res., Miniprint* **1981**, 2537 and references cited.

(4) For review of the utility of the nitroaliphatic compounds in organic synthesis, see: Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1.

(5) Granwell, J. F.; Benson, H. D.; Johnston, J. O.; Petrov, V. *Steroids* **1976**, *27*, 759.

(6) (a) Dauben, W. G.; Bunce, R. A. *J. Org. Chem.* **1983**, *48*, 4642. (b) Dauben, W. G.; Gerdes, J. M. *Tetrahedron Lett.* **1983**, *24*, 3841. (c) Matsumoto, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 770; **1980**, *19*, 1013.

(7) For most recent examples of the concise reviews of high pressure reactions, see: le Noble, W. J. *Chem. Unserer Zeit* **1983**, *17*, 152. Welzel, P. *Nachr. Chem. Techn. Lab.* **1983**, *31*, 148.

(8) For an example of Michael reaction catalyzed by tetra-*n*-butylammonium fluoride, see: Hashimoto, S.; Matsumoto, K.; Otani, S.; Hayami, J.; Yoshida, H. *Synthesis* **1984**, 164.

0022-3263/84/1949-4543$01.50/0