that was a mixture of two main components that were separated by column chromatography (ether–petroleum ether (1:1) as the eluent). The first eluted component was ***trans*-1-*N*-benzoyl-*N*-[2-(methylthio)phenyl]-2-phenylethenamine (12e)**: 0.38 g; mp 148–149 °C (ethanol); IR (CH_2Cl_2) 1680 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.4 (d, J = 15 Hz, 1 H), 6.9–7.6 (m, 14 H), 8.0 (br d, J = 15 Hz, 1 H). The second eluted component was **1-phenyl-1-[[2-(benzoylmethylamino)phenyl]thio]ethene (16c)**: 0.28 g; oil; IR (CH_2Cl_2) 1670 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.4 (s, 3 H), 5.4 (s, 1 H), 5.7 (s, 1 H), 6.5–7.7 (m, 14 H).

(B) Quenching with NH_4Cl. A solution of **4** (2 g, 6.04 mmol) in 40 mL of THF was treated with LDA (7.25 mmol) as above. After 45 min at −78 °C the reaction mixture was quenched with aqueous NH_4Cl and allowed to warm to room temperature. Dilution with ether and the usual workup gave a residue (2.1 g) that was a mixture of two main products which were separated by column chromatography (ether–petroleum ether (3:7) as the eluent). The first-eluted product was **1-phenyl-1-[[2-(benzoylamino)phenyl]thio]ethene (16d)**: 0.86 g; mp 66–68 °C (ether–petroleum ether); IR (CH_2Cl_2) 3385 (NH), 1680 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.7 (s, 1 H), 5.4 (s, 1 H), 7.0–7.9 (cm, 13 H), 8.7 (d, 1 H), 9.1 (br s, 1 H, slow exchange with D_2O). The second-eluted product was **bis(*N*-styryl-*N*-benzoylanilin-2-yl) disulfide (12f)**: 0.71 g; mp 183–185 °C (ethanol); IR (CH_2Cl_2) 1660 (C=O), 1600 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.5 (d, 1 H, J = 14 Hz), 6.9–7.6 (m, 14 H), 8.1 (br d, 1 H, J = 14 Hz); MS, m/e 330 ($M^+/2$).

Reaction of 4-Benzoyl-2,2-dichloro-2,3-dihydro-4*H*-1,4-benzothiazine (8) with LDA. A solution of **8** (0.35 g, 1.1 mmol) in 10 mL of THF was added dropwise at −60 °C to a stirred solution of LDA (2.2 mmol) in 15 mL of THF prepared as above. After 15 min the reaction mixture was warmed to room temperature and NH_4Cl added. Extraction with ether, drying over Na_2SO_4, and evaporation of the solvent left a residue (0.27 g). TLC (ether–petroleum ether (7:3) as the eluent) indicated the presence of one product, which was purified by column chromatography. Its structure is consistent with **4-benzoyl-2-chloro-4*H*-1,4-benzothiazine (18)**: 0.25 g; oil; IR (neat) 1665 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) does not allow to one distinguish between vinylic and aromatic protons. Elemental analysis is in agreement.

Reaction of 4-(Trifluoroacetyl)-2,3-dihydro-4*H*-1,4-benzothiazine (9) with LDA. A solution of **9** (1 g, 4 mmol) in 15 mmol of THF was added to a stirred solution of LDA (5.0 mmol) in 15 mL of THF at −78 °C. After 30 min 0.5 mL of MeI was added and the reaction mixture allowed to warm to room temperature. Dilution with ether (50 mL) and the usual workup left a residue (0.98 g). TLC showed the presence of three main products which were separated by column chromatography (ether–petroleum ether (1:9) as the eluent). The first eluted component was **[[2-[(trifluoroacetyl)amino]phenyl]thio]-ethene (16e)**: 0.06 g; oil; IR (CH_2Cl_2) 3400 (NH), 1660 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.85 (d, 1 H, J = 16 Hz), 5.2 (d, 1 H, 9 Hz), 6.0–6.4 (q, 1 H, J = 16, 9 Hz), 7.0–7.6 (m, 4 H), 8.3 (d, 1 H), 8.9 (br s, 1 H, exchanges slowly with D_2O). The second-eluted component was ***N*-(trifluoroacetyl)-*N*-[2-(methylthio)-phenyl]ethenamine (12g)**: 0.2 g; oil; IR (CH_2Cl_2) 1660 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3 H), 4.1 (d, 1 H, J = 15 Hz), 4.6 (d, 1 H, J = 9 Hz), 7.0–7.7 (cm, 5 H, 4 aromatic protons and 1 vinylic). The third eluted compound was **4*H*-2,3-dihydro-1,4-benzothiazine (19)**: 0.29 g; oil; IR and ^1H NMR consistent.

Reaction of 4-Formyl-2,3-dihydro-4*H*-1,4-benzothiazine (10) with LDA. A solution of **10** (1 g, 5.6 mmol) in 15 mL of THF was added dropwise to a stirred solution of LDA (7.0 mmol) at −78 °C. After 15 min 0.8 mL of MeI was added and the reaction mixture allowed to warm to room temperature. Dilution with ether and the usual workup afforded a residue (1.2 g) that was a mixture of three products. Separation was accomplished by column chromatography (ether–petroleum ether (1:1) as the eluent). The first-eluted product was **4-methyl-2,3-dihydro-4*H*-1,4-benzothiazine (11)**: 0.12 g; oil; IR and ^1H NMR consistent. The second eluted product was **4*H*-2,3-dihydro-1,4-benzothiazine (19)**: 0.34 g; oil; IR and ^1H NMR consistent. The third eluted material (0.18 g; oil) was not identified.

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Registry No. 1, 6397-17-7; **2**, 87011-99-2; **3**, 87012-00-8; **4**, 87012-01-9; **5**, 87012-02-0; **6**, 87012-03-1; **7**, 87012-04-2; **8**, 87039-14-3; **9**, 87012-05-3; **10**, 76800-99-2; **11**, 6397-11-1; **12a**, 87012-06-4; **12b**, 87012-07-5; **12c**, 87012-08-6; **12d**, 87012-09-7; (*E*)-**12e**, 87012-10-0; **12f**, 87012-11-1; **12g**, 87012-12-2; **13a**, 72889-12-4; **13b**, 87012-13-3; **16a**, 87012-14-4; (*E*)-**16b**, 87012-21-3; (*Z*)-**16b**, 87012-15-5; **16c**, 87012-16-6; **16d**, 87012-17-7; **16e**, 87012-18-8; **18**, 87012-19-9; **19**, 3080-99-7; **22**, 7028-57-1; **23**, 87012-20-2; **24**, 58960-00-2; **25**, 83523-72-2; **26**, 25069-67-4; **27**, 66234-07-9; **28**, 25069-64-1; 2-aminobenzenethiol, 137-07-5; α-chloropropionic acid, 598-78-7.

Oxidative Decyanation of Secondary Nitriles to Ketones

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Procedures for the oxidative decyanation of secondary nitriles to ketones involve (1) iodination of *N*-(trialkylsilyl)ketenimines derived from secondary nitriles and subsequent hydrolysis of the α-iodo nitriles with silver oxide, (2) addition of nitrosobenzene to *N*-(trialkylsilyl)ketenimines, (3) conversion of secondary nitriles to α-(phenylthio) nitriles and subsequent hydrolysis with *N*-bromosuccinimide in aqueous acetonitrile, and (4) preparation of α-hydroperoxy nitriles by direct oxygenation of anions of secondary nitriles and subsequent reductive hydrolysis with stannous chloride followed by sodium hydroxide. The latter general procedure was applied to various secondary nitriles bearing dialkyl, aryl and alkyl, and diaryl substituents to provide ketones in good yield and was extended to the oxidative decyanation of α,β-unsaturated nitriles to furnish α,β-unsaturated ketones.

Kharasch and Sosnovsky[1] first demonstrated that secondary nitriles **1** would trap molecular oxygen in the presence of a base to provide ketones **2**. The selection of sodium methoxide in methanol limited the scope of this oxygenation procedure to the relatively acidic, aryl-substituted acetonitriles. For example, diphenylacetonitrile furnished benzophenone in 92% yield, but isobutyronitrile afforded only trace amounts of acetone. The authors suggested that the anion of diphenylacetonitrile trapped oxygen to form an α-hydroperoxy nitrile **3** which ultimately gave benzophenone. Subsequent reports on the aut-

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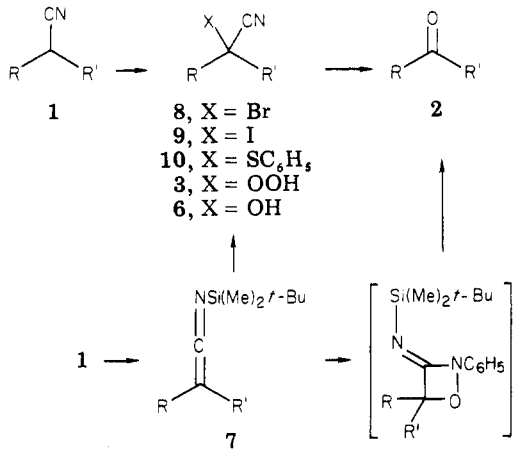
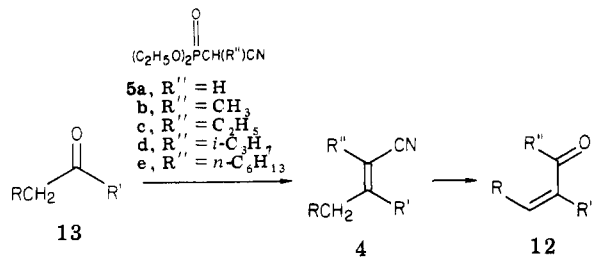
0022-3263/83/1948-4087$01.50/0

Scheme I



Scheme II



oxidation of nitriles focused either on mechanism[2] or on synthetic applications.[3]

In 1973, we initiated a program to develop a general oxidative decyanation procedure to convert secondary nitriles **1** to ketones **2** as shown in Scheme I. We explored a variety of different approaches[4-6] and ultimately developed a general method involving the direct oxygenation of anions of secondary nitriles. We now report recent results as well as detailed accounts of these oxidative decyanation procedures which have enjoyed some success in organic synthesis.[7]

Results and Discussion

The secondary nitriles **1** required for this study were prepared by the following methods: (1) nucleophilic substitution by sodium cyanide on a secondary alkyl halide;[8] (2) alkylation of a primary nitrile;[9] (3) reduction of an α,β-unsaturated nitrile;[10] (4) dehydration of an appropriate carboxamide; and (5) Diels–Alder reaction using acrylonitrile. A summary of the procedures and yields for the secondary nitriles listed in Table I appears in the Experimental Section.

The α,β-unsaturated nitriles **4** required for this study were prepared by using the phosphonate Wittig reaction[11] as shown in Scheme II. The necessary phosphonate reagents **5** were, in turn, prepared from various α-bromo carboxamides according to a published procedure[12] involving sequential dehydration and Arbusov reactions. Alternate approaches involving either the direct bromination of primary nitriles[13] to obtain the requisite α-bromo nitrile intermediates or the alkylation of the anion of phosphonate **5a** were less successful,[14] particularly in large-scale preparations, than the route that we have devised. A summary of the procedures and yields for the preparation of these phosphonates **5** appears in the Experimental Section.

Procedure A. Initially, we anticipated that a three-step process involving the α halogenation of nitrile **1**, substitution of the halogen by hydroxide, and conversion of cyanohydrin **6** to ketone **5** would effect the desired oxidation. At the time that we initiated work in this area, several groups had reported the successful α chlorination[15] or α bromination[15b] of secondary nitriles and subsequently the conversion of α-halo nitriles to ketones.[15c,d,f] We sought to prepare various α-iodo nitriles[16] directly from secondary nitriles, but the direct iodination of secondary nitriles proved unworkable. Ultimately, we resorted to the initial conversion of secondary nitriles to *N*-(*tert*-butyldimethylsilyl)ketenimines[17] **7** and subsequent halogenation[18] of **7** with either bromine or iodine to afford α-halo nitriles[4] **8** and **9**, respectively, as shown in Scheme I. Unfortunately, conversion of these α-halo nitriles to ketones by using sodium hydroxide in dimethyl sulfoxide[15c,d] gave only low yields of the desired ketones. However, treatment of the α-iodo nitriles **9**, but not the α-bromo nitriles **8**, with silver oxide rather than sodium hydroxide led to the desired ketones **2**. This methodology was limited by two factors.

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(18) Halogenation of *N*-arylketenimines led to α-haloimidoyl halides: Stevens, C. L.; French, J. C. *J. Am. Chem. Soc.* **1953**, *75*, 657.

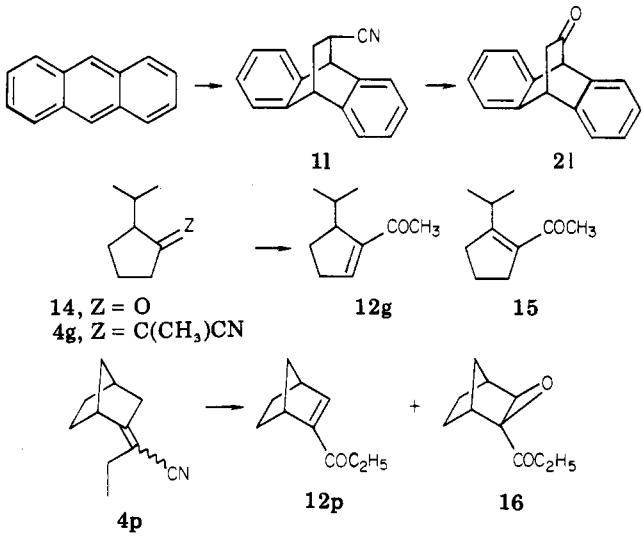
As shown in Table I, this three-step sequence proceeded in overall yields of only 43–64% from nitrile 1 to ketone 2 and, consequently, held limited appeal in any multistep synthetic scheme. Second, and most important, this process succeeded only for nitriles bearing at least one aromatic group. The restricted scope of this process presumably derived from the S_N1 nature of the iodide-substitution reaction leading to the cyanohydrin 6. Although recent interest[19] in the influence of cyano groups on carbocations would suggest some resonance delocalization of charge by the cyano group, this effect alone was not sufficient to favor cyanohydrin formation without the added, stabilizing influence of an aromatic group.

Procedure B. On the basis of literature precedent involving the oxidation of *N*-arylketenimines, we also examined alternate routes using *N*-(*tert*-butyldimethylsilyl)ketenimines 7 for effecting oxidative decyanation. We briefly explored the peracid oxidation[20] and nitrosobenzene [2 + 2] cycloaddition[21] reactions of 7. Although the *m*-chloroperoxybenzoic acid oxidation of **7p**, for example, in the presence of sodium carbonate/dicyclohexyl-18-crown-6 gave only a 37% yield of acetophenone (**2p**), the addition of 2 equiv of recrystallized nitrosobenzene to ketenimine **7p** in chloroform led to acetophenone (**2p**) in 87% yield possibly via the intermediate shown in Scheme I. Other ketenimines, however, failed to match this yield in analogous reactions with nitrosobenzene, and further work on this approach was discontinued.

Procedure C. We next developed an oxidative decyanation procedure which involved α-(phenylthio) nitriles[22] **10** as key intermediates. In this case, the phenylsulfenylation of secondary nitriles involved either the direct trapping of nitrile anions with phenylsulfenyl chloride[27] (**11**) or the addition of **11** to the *N*-(*tert*-butyldimethylsilyl)ketenimines 7 as shown in Scheme I. The former procedure was more convenient and proceeded in higher overall yield than the ketenimine route. Hydrolysis of the α-(phenylthio) nitriles **10** proceeded when using mercuric chloride in *N*-chlorosuccinimide or, preferably, *N*-bromosuccinimide in aqueous acetonitrile to give the desired ketones 2. The latter reagent promoted electrophilic aromatic substitution only in the case of 2-(4-biphenyl)-propionitrile (**1cc**) which afforded a 75% yield of 4-acetyl-4′-bromobiphenyl.[28] However, the overall oxidative decyanation sequence was again restricted to the preparation of ketones 2 bearing at least one aromatic group.

Procedure D. Kulp[3] reported that dimethyl sulfoxide served as both the solvent and oxidizing agent in the conversion of diarylacetonitriles to diaryl ketones using potassium carbonate as a base. In reproducing this work, we noted the absence of significant amounts of dimethyl sulfide and the failure of Kulp's procedure when the reactions were conducted in a nitrogen atmosphere. Consequently, Kulp's procedure[3] represented a variation of Kharasch's autoxidation procedure in which oxygen and not dimethyl sulfoxide was the oxidizing agent. The yields for the oxidative decyanation of diarylacetonitriles using Kulp's procedure were good, but the method was severely limited in scope.

Scheme III



Procedure E. Since it was clear that substitution reactions leading from α-hetero-substituted nitriles to cyanohydrins were severely restricted in scope, we explored the direct oxygenation of nitriles. Secondary nitrile anions generated by using lithium diisopropylamide at −78 °C trapped molecular oxygen to afford α-hydroperoxy nitriles 3. Subsequent reduction of 3 to the cyanohydrins 6 using stannous chloride[29] and exposure of the cyanohydrins to aqueous base liberated the desired ketones 2. Both the intermediate α-hydroperoxy nitriles[30,31] 3 and the cyanohydrins[32] 6 were, on occasion, isolated. This oxidative decyanation procedure proved more general than either the α-iodo or α-(phenylthio) nitrile approaches. A variety of secondary nitriles bearing dialkyl, aryl and alkyl, or dialkyl substituents were transformed to ketones 2 in good yields as shown in Table I. This method could not, however, be extended to the preparation of aldehydes from primary nitriles or to the preparation of carboxylic acids from malononitriles.[33,34]

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(22) α-(Arylthio) and α-(alkylthio) nitriles have been prepared by numerous routes including (1) nucleophilic substitution of α-halo nitriles or cyanohydrin tosylates,[23] (2) acid-catalyzed substitution with α-chloro sulfides or dithioketals and mercuric cyanide,[24] (3) addition of cyanide to thioketones and S-alkylation,[25] and (4) sulfenylation of nitriles with disulfides, thiocyanates or sulfur/alkyl halides.[26]
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(32) For examples as well as a study of the stereoselectivity of the nitrile to cyanohydrin conversion in conformationally anchored systems, see: Freerksen, R. W.; Watt D. S. *Synth. Commun.* **1976**, *6*, 447.
(33) Consonant with our findings, the selenium dioxide oxidation of (2-chlorophenyl)acetonitrile gave a low yield of 2-chlorobenzoic acid: Mel'nikov, N. N.; Baskakov, Yu. A. *Dokl. Acad. Nauk SSSR* **1952**, *85*, 337; *Chem. Abstr.* **1953**, *47*, 7461*f*. Aurich[2] also investigated the autoxidation of phenylacetonitrile to benzoic acid but did not specify the yield.

Table I. Oxidative Decyanation of Secondary Nitriles RR'CHCN (1) to Ketones RCOR' (2)

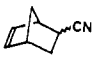
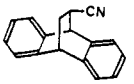
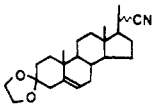
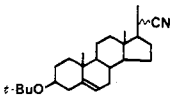
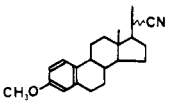
compd	R	R'	method[a]	isolated yield of 2, %
a	CH_3	n-C_6H_{13}	D	0
			E	67
b	CH_3	$(CH_2)_3C_6H_5$	E	59
c	CH_3	c-C_6H_{11}	E	78[d]
d	CH_3	$CH_2C_6H_5$	D	0[h]
			E	82[d]
e	CH_3	C_6H_4-2-CH_3	E	70
f	$CH_2C_6H_5$	c-C_5H_9	E	70[d]
g	$CH_2C_6H_5$	$CH_2C_6H_5$	D	0[h]
			E	90[d]
h	$CH_2C_6H_5$	n-C_4H_9	E	83[d]
i			E	64[d,e]
j			E	65[f]
k			E	65
l			E	56
m			E	69[g]
n			E	70
o			E	74
p	C_6H_5	CH_3	A	63[c]
			B	87[b]
			C	91
			D	60[h]
			E	86[d]
q	C_6H_5	C_2H_5	A	76[c]
			C	70[b]
			E	69[d]
r	C_6H_5	n-C_3H_7	E	70
s	C_6H_5	i-C_3H_7	A	64[c]
			B	37
			C	80[b]
			E	81[d]
t	C_6H_5	n-C_4H_9	E	78
u	C_6H_5	i-C_5H_{11}	E	72
v	C_6H_5	$CH_2CH_2C(CH_3)_3$	E	66
w	C_6H_5	$(CH_2)_3C_6H_5$	E	68
x	C_6H_5	n-C_8H_{17}	A	59[c]
			C	75[b]
y	C_6H_5	c-C_6H_{11}	C	87[b]
			D	36[h]
			E	74[d]
z	C_6H_4-4-F	CH_3	A	57[c]
			C	83[b]
			E	92[d]
aa	C_6H_4-4-Cl	CH_3	A	43[c]
			C	88[b]
			E	79[d]
bb	C_6H_4-4-OCH_3	CH_3	C	74[b]
cc	C_6H_4-4-C_6H_5	CH_3	D	60[h]
			E	82[d]
dd	1-$C_{10}H_7$	CH_3	A	45[c]
			C	45[c]
			E	80[d]
ee	C_6H_5	C_6H_5	A	57[c]
			C	88[b]
			D	88[h]
			E	92[d]

Table I (*Continued*)

compd	R	R'	method[a]	isolated yield of 2, %
ff	C_6H_4-4-OCH_3	C_6H_5	D	90[h]
gg	C_6H_4-4-NO_2	C_6H_5	D	86[h]

[a] Procedure A: (1) LDA, (2) t-$C_4H_9Si(CH_3)_2Cl$, (3) I_2, (4) Ag_2O. Procedure B: (1) LDA, (2) t-$C_4H_9Si(CH_3)_2Cl$, (3) $C_6H_5N{=}O$. Procedure C: (1) n-C_4H_9Li, (2) C_6H_5SCl (3) NBS, aqueous CH_3CN. Procedure D: K_2CO_3, O_2, Me_2SO. Procedure E: (1) LDA, (2) O_2, (3) $SnCl_2$, aqueous HCl, (4) NaOH. [b] Reference 5. [c] Reference 4. [d] Reference 6. [e] Isolated as the 2,4-dinitrophenylhydrazone derivative. [f] Isolated as 2-phenyl-2-cyclohexenone. [g] Isolated as progesterone following treatment with aqueous acid. [h] See ref 3.

The sequential application of a Diels–Alder reaction using acrylonitrile and an oxidative decyanation would formally render acrylonitrile as a "ketene equivalent". Indeed, this sequence, illustrated for anthracene in Scheme III, was employed with 1-phenyl-1,3-butadiene, cyclopentadiene, and anthracene to afford the ketones **2j–l** in good overall yield. The merit in this particular approach rests largely on the availability of acrylonitrile relative to other "ketene equivalents" such as α-chloro-[35] and α-acetoxyacrylonitrile.[36]

We further extended this oxidative decyanation reaction to α,β-unsaturated nitriles **4** in order to prepare α,β-unsaturated ketones **12** as shown in Scheme II. Formally, the overall transformation of the ketone **13** to the α,β-unsaturated ketone **12** in Scheme II involved a condensation–dehydration of the ketone **13** with an acyl anion equivalent.[37] The procedure developed for the oxidative decyanation of secondary nitriles **1** was suitable for the oxidative decyanation of α,β-unsaturated nitriles **4** provided that hexamethylphosphoramide was employed as a cosolvent. As illustrated by the results in Table II, there are two limitations to the scope of this oxidative decyanation: (1) the method fails for the preparation of α,β-unsaturated *aldehydes* from nitriles such as **4h** and (2) the method fails for the preparation of α,β-unsaturated ketones **12** having *two* β-alkyl substituents such as **12e**. This latter limitation can, however, be turned to some advantage in the synthesis of α,β-unsaturated ketones **12** from unsymmetrical ketones **13**. For example, 2-isopropylcyclopentanone (**14**) was converted to the α,β-unsaturated nitrile **4g** shown in Scheme III, and the oxidative decyanation of **4g** furnished exclusively **12g** and none of the isomeric ketone **15**. Finally, in cases where the yields of α,β-unsaturated ketones were disappointing, we found that a fraction of **4** was diverted to the production of γ-hydroxy-α,β-unsaturated nitriles[38] or, in the case of **4p**, to an α,β-epoxy ketone **16** as shown in Scheme III.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 337 or a Beckman Microlab 600 spectrophotometer. The abbreviation TF denotes thin film. NMR spectra were determined on a Varian A-60A, Varian EM-390, or JEOL 270 MHz SC spectrometer. Mass spectra were determined on a Varian MAT CH5 or Du Pont CEC 21-10B mass spectrometer. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Unless otherwise specified, silica gel chromatography was performed on 2-mm-thick, 20 × 20 cm, Merck silica gel F254 plates.

Procedure A. To a solution of 1.1 mmol of lithium diisopropylamide in 2.5 mL of anhydrous THF at −78 °C under a nitrogen atmosphere was added 145 mg (1.0 mmol) of 2-phenylbutyronitrile (**1q**) in 1.0 mL of anhydrous THF. The solution was stirred for ca. 60 min. To the lithionitrile solution was added 316 mg (2.1 mmol, 2.1 equiv) of *tert*-butyldimethylsilyl chloride in 1.0 mL of anhydrous THF. The solution was stirred for 30 min at −78 °C and 60 min at 25 °C. The solvents were evaporated at reduced pressure, and the product was evaporatively distilled at 135–140 °C (oven temperature, 0.25 mm) to afford 244 mg (94%) of yellow *N*-(*tert*-butyldimethylsilyl)ketenimine **7q**. To 259 mg (1.0 mmol) of ketenimine **7q** in 1.0 mL of THF at 0 °C was added 280 mg (1.1 mmol, 1.1 equiv) of iodine in THF. The dark brown solution was stirred for 15 min at 0 °C. To this solution was added 1.16 g (5.0 mmol, 2.5 equiv) of freshly prepared, moist silver oxide. The mixture was refluxed for 30 min, cooled, and filtered through a pad of Celite 545. The Celite pad was thoroughly washed with three 20-mL portions of ether. The ethereal solutions were combined, washed with brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated to afford 590 mg of yellow oil from which 108 mg (81% from **7q**; 76% from **1q**) of propiophenone (**2q**) was isolated by using Girard's "T" reagent.[39]

Procedure B. To 214 mg (2.0 mmol) of recrystallized nitrosobenzene in 2 mL of chloroform under a nitrogen atmosphere was added 245 mg (1.0 mmol) of ketenimine **7p** (prepared from 2-phenylpropionitrile (**1p**) as described in procedure A) in 2 mL of chloroform. The solution was stirred for 24 h at 25 °C, diluted with ether, washed successively with 1 N hydrochloric acid, water, and brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated to afford a highly colored, crude product from which 103 mg (87%) of acetophenone (**2p**) was isolated by using Girard's "T" reagent.[39]

Procedure C. To 636 mg (4 mmol) of isopropylphenylacetonitrile (**1s**) in 6.4 mL of anhydrous THF at −78 °C under a nitrogen atmosphere was added 1.76 mL of 2.29 M (4.0 mmol) *n*-butyllithium in hexane followed by 0.54 mL (4.6 mmol) of benzenesulfenyl chloride. The solution was stirred for 30 min at −78 °C and 30 min at 25 °C. The product was diluted with ether, washed successively with 1 M hydrochloric acid, water, and

(34) For recent reports of nitrile anion oxidations that permit the conversion of primary nitriles to cyanohydrins, see: (a) Vedejs, E.; Telschow, J. E. *J. Org. Chem.* **1976**, *41*, 740. (b) DiBiase, S. A.; Wolak, R. P., Jr.; Dishong, D. M.; Gokel, G. W. *J. Org. Chem.* **1980**, *45*, 3630.

(35) (a) Paasivirta, J.; Krieger, H. *Suom. Kemstil. B* **1965**, *38*, 182; *Chem. Abstr.* **1966**, *64*, 4965g. (b) Paasivirta, J. *Suom. Kemstil. A* **1966**, *39*, 120. (c) Krieger, H.; Masar, S. E. *Ibid.* **1966**, *39*, 119. (d) Corey, E. J.; Koelliker, U.; Neuffer, J. *J. Am. Chem. Soc.* **1971**, *93*, 1489. (e) Damiano, J.; Geribaldi, S.; Torri, G.; Azzaro, M. *Tetrahedron Lett.* **1973**, 2301. (f) Corey, E. J.; Shiner, C. S.; Volante, R. P.; Cyr, C. R. *Ibid.* **1975**, 1161. (g) Monti, S. A.; Chen, S.-C.; Yang, Y.-L.; Yuan, S.-S.; Bourgeois, O. P. *J. Org. Chem.* **1978**, *43*, 4062.

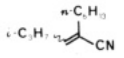
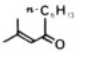
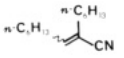
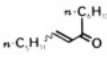
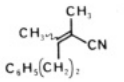
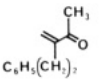
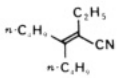
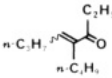
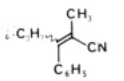
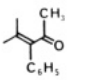
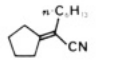
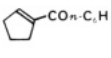
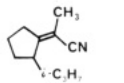
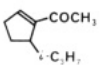
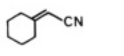
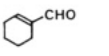
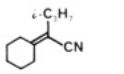
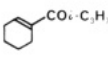
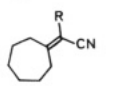
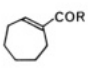
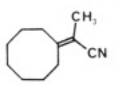
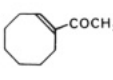
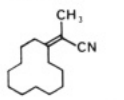
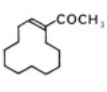
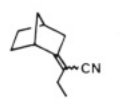
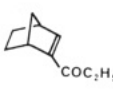
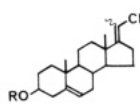
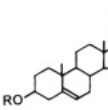
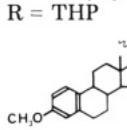
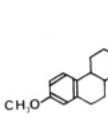
(36) Bartlett, P. D.; Tate, B. E. *J. Am. Chem. Soc.* **1956**, *78*, 2473.

(37) For an alternate approach using 1,3-dithianes as the acyl carbanion equivalent, see: Seebach, D.; Kolb, M.; Grobel, B.-T. *Tetrahedron Lett.* **1974**, 3171.

(38) For studies leading to γ-hydroxy-α,β-unsaturated esters, see: (a) Ortiz de Montellano, P. R.; Hsu, C. K. *Tetrahedron Lett.* **1976**, 4215. (b) Trost, B. M.; Rigby, J. H. *J. Org. Chem.* **1978**, *43*, 2938.

(39) Wheeler, O. H. *Chem. Rev.* **1962**, *62*, 205. The following procedure was used to isolate ketone products from oxidative decyanation experiments and was conducted on a 1.0-mmol scale. To the crude product containing ketone was added 5 mL of 0.4 M Girard "T" reagent in methanol followed by 0.5 mL of glacial acetic acid. The solution was refluxed for 30 min, cooled, and diluted with 8 mL of 1 M aqueous sodium hydroxide and 30 mL of water. The solution was extracted with two 20-mL portions of ether. The ethereal solutions were then extracted with 5 mL of water, and the ethereal solutions were discarded. The combined aqueous solutions were acidified with 10 mL of 3 M hydrochloric acid and extracted with two 20-mL portions of ether. The combined ethereal solutions were washed with 10 mL of water, two 10-mL portions of saturated sodium carbonate solution, and 10 mL of brine, dried over anhydrous magnesium sulfate, and concentrated to afford the ketone product. (Trial experiments demonstrated that >95% of a pure ketone was recovered after subjecting it to the above procedure.)

Table II. Oxidative Decyanation of α,β-Unsaturated Nitriles 4 to Ketones 12

compd	nitrile 4	ketone 12	isolated yield of 12, %
a			6[a]
b			62[a]
c			58
d			44[a]
e			0[a]
f			57[a]
g			69[a]
h			0[a]
i			45[a]
			
j	R = CH_3		57[a]
k	R = C_2H_5		70[a]
l	R = i-C_3H_7		55[a]
m	R = n-C_6H_{13}		72[a]
n			74[a]
o			81[a]
p			17
			
q	R = t-C_4H_9		74[a]
r	R = THP		72[a]
s			78[a]

[a] Wroble, R. R.; Watt, D. S. *J. Org. Chem.* **1976**, *41*, 2939.

brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on silica gel in 1:9 ether–hexane to provide 1.09 g (85%) of **10s**. To 267 mg (1.0 mmol) of **10s** in 5 mL of 25% aqueous acetonitrile was added 1.78 g (10 mmol) of recrystallized *N*-bromosuccinimide. The reaction was stirred for 1.5 h and quenched with saturated sodium sulfite solution and 2 M sodium hydroxide solution. Following an ether extraction, the product was chromatographed, as described above, to afford 139 mg (94% from **10s**; 80% from **1s**) of isobutyrophenone (**2s**).

Procedure D. To 223 mg (1 mmol) of (*p*-methoxyphenyl)-phenylacetonitrile (**1ff**) in 9.5 mL of dimethyl sulfoxide under an oxygen atmosphere was added 0.5 mL of 4 M potassium carbonate in water. The mixture was stirred for 24 h at 25 °C, quenched with 25 mL of 1 M hydrochloric acid, and extracted with 50 mL of ether. The ether solution was washed successively with water and brine and dried over anhydrous magnesium sulfate. The product was chromatographed on silica gel in 1:3 ether–hexane to afford 190 mg (90%) of *p*-methoxybenzophenone (**2ff**).

Procedure E. To a solution of 1.1 mmol of lithium diisopropylamide in 3.0 mL of anhydrous THF at −78 °C under a nitrogen atmosphere was added 145 mg (1.0 mmol) of 2-methyl-3-phenylpropionitrile (**1d**) in 1.0 mL of THF. Dry oxygen gas was bubbled (250 mL/min) into the lithionitrile solution for 30 min at −78 °C. The reaction was quenched with 2 mL of 1 M stannous chloride in 2 M hydrochloric acid solution and allowed to stir for 30 min at 0 °C. The product was diluted with ether, washed successively with water, 1 M sodium hydroxide solution, water, and brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on silica gel in 1:3 ether–hexane to afford 110 mg (82%) of phenylacetone (**2d**).

Summary of Methods of Preparation, Yields, Physical Constants, and Spectral Data for Secondary Nitriles 1 in Table I. Although many of the following compounds are reported in the literature, selected spectra data are given for those cases where the data are not readily accessible or are fragmentary. The yields reported in this section were not optimized.

1a: The procedure of Friedman and Shechter[8] was repeated with 2-bromooctane and sodium cyanide to afford **1a**:[40] 70%; bp 98–99.5 °C (25 mm); IR (TF) 4.54 μm (C≡N); NMR ($CDCl_3$) δ 1.31 (d, J = 7 Hz, 3, CH(CN)CH_3), 2.2–2.7 (m, 1, CH(CN)CH_3); mass spectrum (70 eV), m/e (relative intensity) 139 (3), 124 (12), 110 (36), 96 (83), 55 (100).

1b: The procedure of Watt[41] was repeated with propionitrile and 1-bromo-3-phenylpropane to afford, after silica gel chromatography with 1:9 ether–hexane, **1b**: 68%; IR (TF) 4.57 (C≡N), 6.35 μm (aromatic); NMR ($CDCl_3$) δ 1.24 (d, J = 7 Hz, 1, CHCH_3), 7.24 (m, 5, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 173 (21), 158 (17), 91 (100). Anal. ($C_{12}H_{15}N$) C, H.

1c: The procedure of Profitt, Watt, and Corey[10a] was repeated with 2-(cyclohexylidene)propionitrile to afford **1c**: 91%; IR (TF) 4.46 μm (C≡N); NMR (CCl_4) δ 1.30 (d, J = 7 Hz, 3, CHCH_3); mass spectrum (70 eV), m/e (relative intensity) 83 (69), 55 (100). Anal. ($C_9H_{15}N$) C, H.

1d: The procedure of Watt[41] was repeated with 3-phenylpropionitrile and iodomethane to afford, after silica gel chromatography with 1:9 ether–hexane, **1d**:[42] 56%; IR (TF) 4.45 μm (C≡N); NMR ($CDCl_3$) δ 1.2–1.4 (m, 3, CHCH_3), 2.6–3.1 (m, 3, CHCH_2), 7.32 (m, 5, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 145 (17), 90 (100).

1e: The procedure of Watt[41] was repeated with (*o*-methylphenyl)acetonitrile and iodomethane to afford, after silica gel chromatography with 1:3 ether–hexane, **1e**:[43] 63%; IR (TF) 4.47 μm (C≡N); NMR (CCl_4) δ 1.57 (d, J = 7 Hz, 3, CHCH_3), 2.36 (s, 3, aromatic CH_3), 3.96 (q, J = 7 Hz, 1, CHCH_3), 7.1–7.6 (m, 4, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 145 (59), 130 (100), 118 (70), 103 (74).

1f: The procedure of Watt[41] was repeated with 3-phenylpropionitrile and bromocyclopentane to afford **1f**: 51%; bp 116–118.5 °C (0.2 mm); IR (TF) 4.44 μm (C≡N); NMR (CCl_4) δ 2.6–3.0 (m, 3, CHC$H_2C_6H_5$), 7.29 (m, 5, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 199 (9), 91 (100). Anal. ($C_{14}H_{17}N$) C, H.

1g: The procedure of Watt[41] was repeated with 3-phenylpropionitrile and benzyl chloride to afford, after silica gel chromatography in 1:3 hexane–benzene, **1g**:[44] 75%; mp 92–93.5 °C (recrystallized from hexane–chloroform); IR (KBr) 4.47 μm

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(C≡N); NMR ($CDCl_3$) δ 2.8–3.0 (m, 5, $CH(CH_2C_6H_5)_2$), 7.34 (m, 10, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 221 (16), 91 (100).

1h: The procedure of Watt[41] was repeated with 3-phenylpropionitrile and 1-bromobutane to afford **1h**:[45] 60%; bp 92–96.5 °C (0.2 mm); IR (TF) 4.51 μm (C≡N); NMR (CCl_4) δ 2.4–3.0 (m, 3, $CHCH_2C_6H_5$), 7.27 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 187 (6), 91 (100).

1i: The procedure of Rickborn and Jensen[46] was repeated with cyclohexanecarboxamide to afford **1i**,[47] bp 89–90 °C (25 mm) [lit.[47] bp 117–119 °C (90 mm)].

1j: The procedure of Reich and Becker[48a] was repeated with 1-phenyl-1,3-butadiene and acrylonitrile at 100 °C for 72 h in the presence of 1% hydroquinone to afford **1j**: bp 111–114.5 °C (0.4 mm) [lit.[48] bp 119–121 °C (1 mm), 120–125 °C (3–4 mm)].

1k: The procedure of Alder[49] was repeated with cyclopentadiene and acrylonitrile to afford **1k**, bp 88–93 °C (13 mm) [lit.[49] bp 84–89 °C (13 mm)].

1l: The procedure of Brown and Cookson[50c] was repeated with anthracene and acrylonitrile (sealed tube) at ca. 175 °C for 20 h to afford **1l**:[50] 55%; mp 109.5–112 °C (recrystallized from ether) (lit. mp 115–117,[50c] 108–109 °C[50b]).

1m: See ref 12.

1n–o: See ref 51.

1p: commercially available.

1q: The procedure of Watt[41] was repeated with phenylacetonitrile and iodoethane to afford **1q**:[52] 72%; bp 135–138.5 °C (31 mm); IR (TF) 4.44 (C≡N), 6.22 μm (aromatic); NMR (CCl_4) δ 3.73 (t, *J* = 7 Hz, 1, $CH_2CHC_6H_5$), 7.34 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 145 (34), 117 (100).

1r: The procedure of Watt[41] was repeated with phenylacetonitrile and 1-bromopropane to afford **1r**:[53] bp 125–128.5 °C (9 mm); IR (TF) 4.47 (C≡N), 6.25 μm (aromatic); NMR ($CDCl_3$) δ 0.85–1.1 (m, 3, CH_3), 3.75 (t, *J* = 7 Hz, 1, CHC_6H_5), 7.30 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 159 (25), 117 (100).

1s: The procedure of Watt[41] was repeated with phenylacetonitrile and 2-bromopropane to afford **1s**:[54] 73%; bp 140–145 °C (28 mm); IR (TF) 4.53 (C≡N), 6.28 μm (aromatic); NMR (CCl_4) δ 1.02 and 1.07 (2 d, *J* = 6 Hz, 6, $CHCH(CH_3)_2$), 1.8–2.4 (m, 1, $CHCH(CH_3)_2$), 3.60 (d, *J* = 6 Hz, 1, $CHCH(CH_3)_2$), 7.29 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 159 (12), 117 (100).

1t: The procedure of Watt[41] was repeated with phenylacetonitrile and 1-bromobutane to afford **1t**:[54b,55] 50%; bp 90–93 °C (0.5 mm); IR (TF) 4.48 (C≡N), 6.26 μm (aromatic); NMR (CCl_4) δ 0.8–1.1 (m, 3, CH_3), 3.55–3.9 (m, 1, CHC_6H_5), 7.34 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 173 (15), 117 (100).

1u: The procedure of Watt[41] was repeated with phenylacetonitrile and 1-bromo-3-methylbutane to afford **1u**:[54b,56] 65%; bp 97–99 °C (0.45 mm); IR (TF) 4.48 (C≡N), 6.26 μm (aromatic); NMR (CCl_4) δ 0.90 (d, *J* = 6 Hz, 6, $CH(CH_3)_2$), 3.69 (t, *J* = 7 Hz, 1, $CH_2CHC_6H_5$), 7.34 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 187 (19), 172 (21), 117 (100).

1v: The procedure of Watt[41] was repeated with phenylacetonitrile and 1-bromo-3,3-dimethylbutane to afford **1v**: 62%; bp 116–119 °C (1 mm); IR (TF) 4.47 (C≡N), 6.25 μm (aromatic); NMR (CCl_4) δ 0.88 (s, 9, $C(CH_3)_3$), 3.5–3.8 (m, 1, CHC_6H_5), 7.34 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 201 (13), 186 (9), 117 (68), 57 (100). Anal. ($C_{14}H_{19}N$) C, H.

1w: The procedure of Watt[41] was repeated with phenylacetonitrile and 1-bromo-3-phenylpropane to afford **1w**:[56a,57] 56%; mp 76–78 °C (recrystallized from ether); bp 149–153 °C (0.2 mm); IR (TF) 4.48 (C≡N), 6.25 μm (aromatic); NMR (CCl_4) δ 3.5–3.85 (m, 1, CHC_6H_5), 6.9–7.5 (m, 10, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 235 (36), 130 (13), 117 (15), 104 (18), 91 (100).

1x: The procedure of Watt[41] was repeated with phenylacetonitrile and 1-bromooctane to afford **1x**:[54b,56b] 72%; IR (TF) 4.48 (C≡N), 6.25 μm (aromatic); NMR ($CDCl_3$) δ 0.87 (t, *J* = 7 Hz, 3, CH_2CH_3), 1.10–2.00 (m, 14, CH_2), 3.76 (t, *J* = 7.9 Hz, 1, CHCN), 7.32 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 229 (20), 173 (8), 159 (9), 117 (100). Anal. ($C_{16}H_{23}N$) C, H.

1y–aa: commercially available.

1bb: The procedure of Watt[41] was repeated with (4-methoxyphenyl)acetonitrile and iodomethane to afford, after silica gel chromatography with 1:3 ether–hexane, **1bb**:[58] 77%; IR (TF) 4.46 (C≡N), 6.17 μm (aromatic); NMR (CCl_4) δ 1.57 (d, *J* = 7 Hz, 3, $CHCH_3$), 3.78 (s, 3, OCH_3), 6.7–7.3 (m, 4, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 161 (31), 146 (100).

1cc: The procedure of Watt[41] was repeated with 4-(cyanomethyl)biphenyl and iodomethane to afford, after silica gel chromatography with 1:3 ether–hexane, **1cc**:[59] IR (KBr) 4.57 μm; NMR ($CDCl_3$) δ 1.62 (d, *J* = 7 Hz, 3, $CHCH_3$), 3.90 (q, *J* = 7 Hz, 1, $CHCH_3$), 7.3–7.7 (m, 9, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 207 (100), 192 (36).

1dd: The procedure of Watt[41] was repeated with 1-(cyanomethyl)naphthalene and iodomethane to afford, after silica gel chromatography with 1:4 ether–hexane, **1dd**:[60] 66%; IR (TF) 4.47 (C≡N), 6.25 μm (aromatic); NMR (CCl_4) δ 1.64 (d, *J* = 7 Hz, 3, $CHCH_3$), 4.45 (q, *J* = 7 Hz, 1, $CHCH_3$), 7.3–7.9 (m, 7, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 181 (69), 180 (81), 166 (100), 153 (50).

1ee: commerically available.

1ff: See ref 61.

1gg: See ref 62.

Summary of Physical Constants and Spectral Data for Ketones 2 in Table I. 2a: commercially available. **2b**: See ref 63. **2c–e**: commercially available. **2f**: NMR ($CDCl_3$) δ 1.3–2.0 (m, 8, $(CH_2)_4$), 2.7–3.1 (m, 1, $CHCOCH_2$), 3.73 (s, 2, $CHCOCH_2$), 7.31 (s, 5, aromatic H). Anal. ($C_{13}H_{16}O$) C, H. **2g**: commerically available. **2h**: See ref 64. **2i**: commercially available. **2j**: See ref 65. **2k**: See ref 66. **2l**: See ref 67. **2m**: See ref 12. **2n**:

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See ref 51. **2o**: See ref 51. **2p–u**: commercially available. **2v**: See ref 68. **2w**: See ref 69. **2x**: See ref 70. **2y–gg**: commercially available.

Summary of Methods of Preparation, Yields, Physical Constants, and Spectral Data for α,β-Unsaturated Nitriles 4 in Table II. 4a: The procedure of Raggio and Watt[12] was repeated with isobutyraldehyde and phosphonate **5e** to afford **4a**: 66%; R_f 0.63 (1:9 ether–hexane); IR (TF) 4.52 μm (C≡); NMR (CCl_4) δ 0.7–1.2 (m, 9, $CH(CH_3)_2$ and CH_2CH_3), 1.9–2.3 (m, 2, allylic H), 2.5–3.1 (m, 1, $CH(CH_3)_2$), 5.7–6.0 (m, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 179 (13), 164 (24), 136 (69), 122 (34), 95 (100). Anal. ($C_{12}H_{21}N$) C, H.

4b: The procedure of Raggio and Watt[12] was repeated with *n*-heptanal and phosphonate **5e** to afford **4b**: 73%; R_f 0.61 (1:9 ether–hexane); IR (TF) 4.56 (C≡N), 6.12 μm (C=C); NMR ($CDCl_3$) δ 0.90 (m, 6, CH_2CH_3), 2.0–2.6 (m, 4, allylic H), 6.12 (t, J = 8 Hz, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 221 (19), 206 (15), 192 (28), 178 (24), 164 (38), 150 (100). Anal. ($C_{15}H_{27}N$) C, H.

4c: The procedure of Raggio and Watt[12] was repeated with 4-phenyl-2-butanone and phosphonate **5b** to afford **4c**: 71%; R_f 0.6 in dichloromethane; IR (TF) 4.52 (C≡N), 6.11 (C=C), 6.23 μm (aromatic); NMR (CCl_4) δ 1.60, 1.81, 1.99 (3 s, 6, vinylic CH_3 of *E/Z* isomers), 2.2–2.9 (m, 4, CH_2), 6.95–7.35 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 185 (15), 131 (13), 91 (100). Anal. ($C_{13}H_{15}N$) C, H.

4d: The procedure of Raggio and Watt[12] was repeated with 5-nonanone and phosphonate **5c** to afford **4d**: 81%; R_f 0.44 (1:9 ether–hexane); IR (TF) 4.56 (C≡N), 6.19 μm (C=C); NMR (CCl_4) δ 0.8–1.2 (m, 17, CH_2 and CH_3), 2.0–2.6 (m, 6, allylic H); mass spectrum (70 eV), *m/e* (relative intensity) 193 (31), 164 (50), 138 (100), 124 (40), 108 (61). Anal. ($C_{13}H_{23}N$) C, H.

4e: The procedure of Raggio and Watt[12] was repeated with isobutyrophenone and phosphonate **5b** to afford **4e** (88%) as a 1:3 mixture of *E/Z* isomers. For the *E* isomer: R_f 0.25 (1:9 ether–hexane); IR (TF) 4.54 (C≡N), 6.19 (C=C), 6.28 μm (aromatic); NMR (CCl_4) δ 0.97 (d, J = 7 Hz, 6, $CH(CH_3)_2$), 2.02 (s, 3, vinylic CH_3), 2.7–3.3 (m, 1, $CH(CH_3)_2$), 6.9–7.5 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 185 (71), 170 (100), 143 (84), 128 (40), 115 (52). Anal. ($C_{13}H_{15}N$) C, H. For the *Z* isomer: R_f 0.40 (1:9 ether–hexane); IR (TF) 4.53 (C≡N), 6.18 (C=C), 6.27 μm (aromatic); NMR (CCl_4) δ 1.02 (d, J = 7 Hz, 6, $CH(CH_3)_2$), 1.61 (s, 3, vinylic CH_3), 2.9–3.65 (m, 1, $CH(CH_3)_2$), 6.85–7.5 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 185 (88), 170 (100), 143 (68), 128 (30), 115 (42). Anal. ($C_{13}H_{15}N$) C, H.

4f: The procedure of Raggio and Watt[12] was repeated with cyclopentanone and phosphonate **5e** to afford **4f**: 94%; R_f 0.41 (1:9 ether–hexane); IR (TF) 4.56 (C≡N), 6.10 μm (C=C); NMR (CCl_4) δ 0.91 (m, 3, CH_2CH_3), 1.95–2.70 (m, 6, allylic H); mass spectrum (70 eV), *m/e* (relative intensity) 191 (42), 173 (13), 162 (27), 148 (39), 134 (17), 120 (28). Anal. ($C_{13}H_{21}N$) C, H.

4g: The procedure of Raggio and Watt[12] was repeated with 2-isopropylcyclopentanone (**14**) and phosphonate **5b** to afford **4g**: 79%; R_f 0.43 (1:9 ether–hexane); IR (TF) 4.53 (C≡N), 6.11 μm (C=C); NMR (CCl_4) δ 0.85 and 1.00 (2 d, J = 6 Hz, 6, $CH(CH_3)_2$), 1.59–1.86 (m, 4, CH_2), 1.89 (s, 3, vinylic CH_3), 2.00–2.95 (m, 4, $CH(CH_3)_2$ and allylic CH and CH_2); mass spectrum (70 eV), *m/e* (relative intensity) 163 (22), 148 (13), 121 (100). Anal. ($C_{11}H_{17}N$) C, H.

4h: The procedure of Raggio and Watt[12] was repeated with cyclohexanone and phosphonate **5a** to afford **4h**: 89%; IR (TF) 4.50 (C≡N), 6.10 μm (C=C); NMR ($CDCl_3$) δ 1.40–1.88 (m, 6, CH_2), 2.10–2.65 (m, 4, allylic H), 5.09 (s, 1 vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 121 (18), 68 (65), 55 (44), 43 (100).

4i: The procedure of Raggio and Watt[12] was repeated with cyclohexanone and phosphonate **5d** to afford **4i**: 88%; R_f 0.49 (1:9 ether–hexane); IR (TF) 4.55 (C≡N), 6.18 μm (C=C); NMR (CCl_4) δ 1.08 (d, J = 7 Hz, 6, $CH(CH_3)_2$), 1.4–1.9 (m, 6, CH_2), 2.1–2.5 (m, 4, allylic H), 2.5–3.1 (m, 1, $CH(CH_3)_2$); mass spectrum (70 eV), *m/e* (relative intensity) 163 (50), 148 (100), 121 (50), 96 (50). Anal. ($C_{11}H_{17}N$) C, H.

4j: The procedure of Raggio and Watt[12] was repeated with cycloheptanone and phosphonate **5b** to afford **4j**: 95%; R_f 0.50 (1:9 ether–hexane); IR (TF) 4.51 (C≡N), 6.20 μm (C=C); NMR ($CDCl_3$) δ 1.4–2.0 (m, 8, CH_2), 1.83 (br s, 3, vinylic CH_3), 2.25–2.75 (m, 4, allylic H); mass spectrum (70 eV), *m/e* (relative intensity) 149 (65), 134 (28), 93 (55), 67 (100). Anal. ($C_{10}H_{15}N$) C, H.

4k: The procedure of Raggio and Watt[12] was repeated with cycloheptanone and phosphonate **5c** to afford **4k**: 90%; R_f 0.50 (1:9 ether–hexane); IR (TF) 4.55 (C≡N), 6.22 μm (C=C); NMR (CCl_4) δ 1.28 (t, J = 6 Hz, 3, CH_2CH_3), 1.4–2.0 (m, 8, CH_2), 2.0–2.9 (m, 6, allylic H); mass spectrum (70 eV), *m/e* (relative intensity) 163 (39), 148 (20), 134 (24), 106 (32), 67 (100). Anal. ($C_{11}H_{17}N$) C, H.

4l: The procedure of Raggio and Watt[12] was repeated with cycloheptanone and phosphonate **5d** to afford **4l**: 35%; R_f 0.44 (1:9 ether–hexane); IR (TF) 4.58 (C≡N), 6.21 μm (C=C); NMR ($CDCl_3$) δ 1.11 (d, J = 6 Hz, 6, $CH(CH_3)_2$), 1.4–1.9 (m, 8, CH_2), 2.0–3.0 (m, 5, allylic H); mass spectrum (70 eV), *m/e* (relative intensity) 177 (66), 162 (100), 135 (66), 120 (53). Anal. ($C_{12}H_{19}N$) C, H.

4m: The procedure of Raggio and Watt[12] was repeated with cycloheptanone and phosphonate **5e** to afford **4m**: 96%; R_f 0.49 (1:9 ether–hexane); IR (TF) 4.58 (C≡N), 6.21 μm (C=C); NMR ($CDCl_3$) δ 0.7–1.1 (m, 3, CH_2CH_3), 1.1–1.9 (m, 16, CH_2), 2.0–2.9 (m, 6, allylic H); mass spectrum (70 eV), *m/e* (relative intensity) 219 (100), 190 (37), 176 (42), 162 (39), 148 (40). Anal. ($C_{15}H_{25}N$) C, H.

4n: The procedure of Raggio and Watt[12] was repeated with cyclooctanone and phosphonate **5b** to afford **4n**: 88%; R_f 0.43 (1:9 ether–hexane); IR (TF) 4.55 (C≡N), 6.17 μm (C=C); NMR (CCl_4) δ 1.2–2.0 (m, 10, CH_2), 1.75–1.95 (s, 3, vinylic CH_3), 2.1–2.7 (m, 4, allylic H); mass spectrum (70 eV), *m/e* (relative intensity) 163 (60), 148 (33), 96 (51), 81 (100). Anal. ($C_{11}H_{17}N$) C, H.

4o: The procedure of Raggio and Watt[12] was repeated with cyclododecanone and phosphonate **5b** to afford **4o**: 94%; R_f 0.50 (1:9 ether–hexane); IR (TF) 4.52 (C≡N), 6.13 μm (C=C); NMR (CCl_4) δ 1.2–1.8 (m, 18, CH_2), 1.8–1.95 (m, 3, vinylic CH_3), 2.0–2.6 (m, 4, allylic H); mass spectrum (70 eV), *m/e* (relative intensity) 219 (61), 95 (76). Anal. ($C_{15}H_{25}N$) C, H.

4p: The procedure of Raggio and Watt[12] was repeated using norcamphor and phosphonate **5c** to afford **4p**: 89%; IR (TF) 4.52 (C≡N), 6.04 μm (C=C); NMR ($CDCl_3$) δ 1.10 (t, J = 7 Hz, 3, CH_2CH_3), 2.09–2.25 (m, 4, allylic CH_2); mass spectrum (70 eV), *m/e* (relative intensity) 161 (71), 146 (77), 132 (100). Anal. ($C_{11}H_{15}N$) C, H.

4q: See ref 51.

4r: See ref 12.

4s: See ref 51.

Summary of Yields, Physical Constants, and Spectral Data for Phosphonates 5 Used To Prepare α,β-Unsaturated Nitriles 4 in Table II. 2-(Diethylphosphono)acetonitrile (5a): commercially available.

2-(Diethylphosphono)propionitrile (5b): See ref 12.

2-(Diethylphosphono)butyronitrile (5c). The procedure of Raggio and Watt[12] was repeated with 88 g of butyric acid to afford, after recrystallization from acetone, 2-bromobutyramide: 81 g (49%); mp 108–110 °C; IR ($CHCl_3$) 5.93 μm (C=O); NMR ($CDCl_3$, Me_2SO-d_6) δ 1.00 (t, 3, CH_2CH_3), 2.01 (m, 2, $CHCH_2CH_3$), 4.46 (t, 1, CHBr), 7.10 (br s, 2, $CONH_2$); mass spectrum (70 eV), *m/e* (relative intensity) 165 (0.2), 139 (24), 137 (25), 86 (17).

The procedure of Raggio and Watt[12] was repeated with 100 g (0.6 mol) of 2-bromobutyramide and 111 g (0.78 mol, 1.3 eq) of phosphorus pentoxide to afford 68 g (76%) of 2-bromobutyronitrile: bp 69.5–70.5 °C (25 mm); IR (TF) 4.47 μm (C≡N); NMR ($CDCl_3$) δ 1.18 (t, 3, CH_3), 2.15 (m, 2, CH_3CH_2CHBr), 4.31 (t, 1, CHBr); mass spectrum (70 eV), *m/e* (relative intensity) 147 (2), 121 (4).

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The procedure of Raggio and Watt[12] was repeated with 67 g (0.45 mol, 1 equiv) of 2-bromobutyronitrile and 150 g (0.90 mol, 2 equiv) of triethyl phosphite to afford 2-(diethylphosphono)-butyronitrile (**5c**): 72 g (77%); bp 96–98 °C (1 mm); IR (TF) 4.47 μm (C≡N); NMR ($CDCl_3$) δ 1.00–1.60 (m, 9, CH_3), 1.66–2.30 (m, 2, CH_2CH_3), 2.75–3.30 (m, 1, CH_2CHCN), 4.00–4.60 (m, 4, OCH_2CH_3).

2-(Diethylphosphono)-3-methylbutyronitrile (5d). The procedure of Raggio and Watt[12] was repeated with 100 g of 3-methylbutyric acid to afford, after recrystallization from acetone, 56 g (31%) of 2-bromo-3-methylbutyramide: mp 131–132 °C; IR ($CHCl_3$) 5.96 μm (C=O); NMR ($CDCl_3$, Me_2SO-d_6) δ 1.03 (d, 6, $CH(CH_3)_2$), 2.22 (m, 1, $CH(CH_3)_2$), 4.16 (m, 1, CHBr), and 7.05 (br s, 2, $CONH_2$); mass spectrum (70 eV), *m/e* (relative intensity) 179 (1), 139 (98), 137 (100), 100 (54).

The procedure of Raggio and Watt[12] was repeated with 100 g (0.55 mol, 1 equiv) of 2-bromo-3-methylbutyramide and 102 g (0.72 mol, 1.3 equiv) of phosphorus pentoxide to afford 2-bromo-3-methylbutyronitrile: 72 g (81%); bp 79 °C (25 mm); IR (TF) 4.56 μm (C≡N); NMR ($CDCl_3$) δ 1.19 (d, 6, $CH(CH_3)_2$), 2.18 (m, 1, $CH(CH_3)_2$), 4.28 (d, 1, CHBr); mass spectrum (70 eV), *m/e* (relative intensity) 161 (1), 121 (40), 119 (44).

The procedure of Raggio and Watt[12] was repeated with 70.9 g (0.44 mol, 2 equiv) of 2-bromo-3-methylbutyronitrile and 145 g (0.88 mol, 2 equiv) of triethyl phosphite to afford 2-(diethylphosphono)-3-methylbutyronitrile (**5d**): 36.6 g (40%); bp 106.5–108 °C (0.8 mm); IR (TF) 4.47 μm (C≡N); NMR ($CDCl_3$) δ 1.15–1.60 (m, 12, CH_3), 2.80 (m, 1, $CH(CH_3)_2$), 3.15 (d, 1, CHCN), 4.0–4.6 (m, 4, OCH_2CH_3).

2-(Diethyphosphono)octanenitrile (5e). The procedure of Raggio and Watt[12] was repeated with 288 g of octanoic acid to afford, after recrystallization from acetone, 2-bromooctanamide: 79 g (36%); mp 51.5–53 °C; IR ($CHCl_3$) 5.94 μm (C=O); NMR ($CDCl_3$) δ 0.89 (m, 3, $(CH_2)_5CH_3$), 1.0–2.3 (m, 10, $(CH_2)_5CH_3$), 4.32 (t, 1, CHBr), 6.32 (br s, 2, $CONH_2$); mass spectrum (70 eV), *m/e* (relative intensity) 221 (1), 152 (5), 150 (5), 139 (92), 137 (100).

The procedure of Raggio and Watt[12] was repeated with 100 g (0.45 mol, 1 equiv) of 2-bromooctanamide and 83 g (0.59 mol, 1.3 equiv) of phosphorus pentoxide to afford 2-bromooctanenitrile: 64 g (70%); bp 128–130 °C (22 mm); IR (TF) 4.58 μm (C≡N); NMR ($CDCl_3$) δ 0.90 (m, 3, CH_3), 1.00–2.40 (m, 10, $(CH_2)_5CH_3$), 4.33 (t, 1, CHBr); mass spectrum (70 eV), *m/e* (relative intensity) 188 (1), 124 (50), 96 (55), 82 (100).

The procedure of Raggio and Watt[12] was repeated with 73 g (0.36 mol, 1 equiv) of 2-bromooctanenitrile and 119 g (0.72 mol, 2 equiv) of triethyl phosphite to afford 2-(diethylphosphono)-octanenitrile (**5e**): 66 g (70%); bp 136–139 °C (0.6 mm); IR (TF) 4.46 μm (C≡N); NMR ($CDCl_3$) δ 0.6–2.3 (m, 19, CH_3 and CH_2), 2.7–3.2 (m, 1, CHCN), 4.0–4.6 (m, 4, OCH_2CH_3).

Summary of Physical Constants and Spectral Data for *N*-(*tert*-Butyldimethylsilyl)ketenimines 7 Derived from Secondary Nitriles 1 in Table I. 7p: bp 88–91 °C (0.1 mm); spectral data in ref 17f.

7q: bp 95–99 °C (0.15 mm); spectral data in ref 4.

7s: bp 94–100 °C (0.22 mm); IR 4.97 (C=C=N), 6.32 μm (aromatic); NMR (CCl_4) δ 0.27 (s, 6, $Si(CH_3)_2$), 1.02 (s, 9, $SiC(CH_3)_3$), 1.17 (d, *J* = 6.5 Hz, 6, $CH(CH_3)_2$), 2.7 (m, 1, $CH(CH_3)_2$), 6.7–7.3 (m, 5, aromatic H).

7x: bp 148.5–153 °C (0.3 mm); IR (TF) 4.96 (C=C=N), 6.33 μm (aromatic); NMR (CCl_4) δ 0.25 (s, 6, $Si(CH_3)_2$), 1.00 (s, 9, $SiC(CH_3)_3$), 0.8–1.7 (m, 15, $CH_2(CH_2)_6CH_3$), 2.25 (m, 2, $CH_2(CH_2)_6CH_3$), 6.7–7.4 (m, 5, aromatic H).

7z: bp 107–112 °C (0.55 mm); IR (TF) 4.93 (C=C=N), 6.34 μm (aromatic).

7aa: bp 108–114 °C (0.2 mm); IR (TF) 4.95 (C=C=N), 6.33 μm (aromatic); NMR ($CDCl_3$) δ 0.27 (s, 6, $Si(CH_3)_2$), 1.00 (s, 9, $SiC(CH_3)_3$), 1.90 (s, 3, vinylic CH_3), 6.8–7.4 (m, 4, aromatic H).

7dd: bp 128–129 °C (0.2 mm); IR (TF) 4.88 (C=C=N), 6.35 μm (aromatic); NMR ($CDCl_3$) δ 0.23 (s, 6, $Si(CH_3)_2$), 0.93 (s, 9, $SiC(CH_3)_3$), 2.15 (s, 3, vinylic CH_3), 7.1–7.8 (m, 7, aromatic H).

7ee: bp 143–150 °C (0.2 mm); IR (TF) 4.90 (C=C=N), 6.28 μm (aromatic H); NMR ($CDCl_3$) δ 0.32 (s, 6, $Si(CH_3)_2$), 0.99 (s, 9, $SiC(CH_3)_3$), 7.0–7.6 (m, 10, aromatic H).

Summary of Physical Constants and Spectral Data for α-(Phenylthio) Nitriles 10 Derived from Secondary Nitriles 1 in Table I. 10p: IR (TF) 4.50 μm (C≡N, weak); NMR ($CDCl_3$) δ 1.95 (s, 3, CH_3), 7.1–7.6 (m, 10, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 239 (5), 130 (100), 110 (63). Anal. ($C_{15}H_{13}NS$) C, H.

10q: IR (TF) 4.55 μm (C≡N, weak); NMR (CCl_4) δ 1.00 (t, *J* = 7 Hz, 3, CH_2CH_3), 2.24 (q, *J* = 7 Hz, 2, CH_2CH_3), 7.0–7.6 (m, 10, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 253 (7), 144 (100), 116 (43), 110 (89). Anal. ($C_{16}H_{15}NS$) C, H.

10s: IR (TF) 4.55 μm (C≡N, weak); NMR (CCl_4) δ 0.88 and 1.46 (2 d, *J* = 7 Hz, 6, $CH(CH_3)_2$), 2.57 (m, 1, $CH(CH_3)_2$), 7.0–7.5 (m, 10, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 267 (7), 158 (100), 143 (23), 116 (34). Anal. ($C_{17}H_{17}NS$) C, H.

10x: bp 185–190 °C (0.15 mm); IR (TF) 4.52 μm (C≡N, weak); NMR ($CDCl_3$) δ 0.7–1.0 (m, 3, $CH_2(CH_2)_6CH_3$), 1.0–1.6 (m, 12, $CH_2(CH_2)_6CH_3$), 2.0–2.5 (m, 2, $CH_2(CH_2)_6CH_3$), 7.1–7.6 (m, 10, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 337 (1), 228 (28), 120 (44), 117 (100). Anal. ($C_{22}H_{27}NS$) C, H.

10y: IR (TF) 4.50 μm (C≡N, weak); NMR ($CDCl_3$) δ 0.9–2.6 (m, 11, c-C_6H_{11}), 7.0–7.5 (m, 10, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 198 (38), 119 (28), 117 (100). Anal. ($C_{20}H_{21}NS$) C, H.

10z: IR (TF) 4.52 μm (C≡N, weak); NMR (CCl_4) δ 1.93 (s, 3, CH_3), 6.8–7.6 (m, 9, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 257 (3), 148 (100), 121 (31), 110 (53). Anal. ($C_{15}H_{12}FNS$) C, H.

10aa: IR (TF) 4.50 μm (C≡N, weak); NMR ($CDCl_3$) δ 1.97 (s, 3, CH_3), 7.2–7.6 (m, 9, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 275 (27), 273 (83), 164 (100), 110 (54). Anal. ($C_{15}H_{12}ClNS$) C, H.

10bb: IR (TF) 4.50 μm (C≡N, weak); NMR (CCl_4) δ 1.92 (s, 3, CH_3), 3.77 (s, 3, OCH_3), 6.7–7.7 (m, 9, aromatic H). Anal. ($C_{16}H_{15}NOS$) C, H.

10dd: IR (TF) 4.54 μm (C≡N, weak); NMR ($CDCl_3$) δ 2.18 (s, 3, CH_3), 7.0–8.0 (m, 12, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 289 (1), 195 (11), 181 (51), 180 (59), 166 (100), 138 (84). Anal. ($C_{19}H_{15}NS$) C, H.

10ee: IR (TF) 4.56 μm (C≡N, weak); NMR (CCl_4) δ 7.1–7.7 (m, 15, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 189 (100), 147 (82), 138 (44), 131 (42). Anal. ($C_{20}H_{15}NS$) C, H.

Summary of Physical Constants and Spectral Data for α,β-Unsaturated Ketones 12 in Table II. 12a: R_f 0.44 (1:9 ether–hexane); IR (TF) 5.92 (C=O), 6.17 μm (C=C); NMR (CCl_4) δ 0.6–1.8 (m, 11, $(CH_2)_4CH_3$), 1.85 and 2.10 (2 s, 6, vinylic CH_3), 2.30 (m, 2, $COCH_2$), 5.97 (m, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 168 (8), 125 (7), 109 (31), 98 (5), 83 (100). Anal. ($C_{11}H_{20}O$) C, H.

12b: R_f 0.62 in dichloromethane; IR (TF) 5.96 (C=O), 6.14 μm (C=C); NMR ($CDCl_3$) δ 0.88 and 0.89 (2 t, *J* = 6.6 Hz, 6, CH_2CH_3), 6.09 (d, *J* = 15.9 Hz, 1, $COCH$=$CHCH_2$), 6.83 (d of t, *J* = 7.3, 15.9 Hz, 1, $COCH$=$CHCH_2$); mass spectrum (70 eV), *m/e* (relative intensity) 210 (4), 155 (21), 140 (95), 139 (67), 125 (100). Anal. ($C_{14}H_{26}O$) C, H.

12c: R_f 0.52 (1:20 ethyl acetate–dichloromethane); IR (TF) 5.98 (C=O), 6.25 (C=C), 6.70 μm (aromatic); NMR (CCl_4) δ 2.22 (s, 3, $COCH_3$), 2.3–2.9 (m, 4, $(CH_2)_2C_6H_5$), 5.59 and 5.85 (2 s, 2, vinylic H), 7.0–7.3 (m, 5, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 174 (13), 159 (10), 131 (11), 91 (100). Anal. ($C_{12}H_{14}O$) C, H.

12d: isolated as a mixture of *E*/*Z* isomers; R_f 0.49 (dichloromethane); IR (TF) 5.98 (C=O), 6.11 μm (C=C); NMR (CCl_4) δ 0.7–1.7 (m, 15, CH_2 and CH_3), 2.0–2.5 (m, 4, allylic H), 2.61 (q, *J* = 7 Hz, 2, $COCH_2CH_3$), 6.52 (t, *J* = 7 Hz, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 182 (20), 153 (100), 139 (14). Anal. ($C_{12}H_{22}O$) C, H.

12f: R_f 0.76 (dichloromethane); IR (TF) 6.00 (C=O), 6.20 μm (C=C); NMR (CCl_4) δ 0.65–1.0 (m, 3, CH_2CH_3), 1.0–2.8 (m, 16, CH_2), 6.60 (m, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 180 (13), 110 (63), 95 (100). Anal. ($C_{12}H_{20}O$) C, H.

12g: isolated as a mixture of *E*/*Z* isomers; R_f 0.42 (dichloromethane); IR (TF) 6.01 (C=C), 6.22 μm (C=C); NMR ($CDCl_3$) δ 0.67 and 0.93 (2 d, *J* = 7 Hz, 6, $CH(CH_3)_2$), 1.6–3.2 (m, 5, CH and CH_2), 2.24 (s, 3, $COCH_3$), 6.65–6.75 (m, 1, vinylic H); mass

spectrum (70 eV), *m/e* (relative intensity) 152 (54), 110 (57), 109 (61), 95 (73), 67 (100). Anal. ($C_{10}H_{16}O$) C, H.

12i: R_f 0.37 (dichloromethane); IR (TF) 6.01 (C=O), 6.12 μm (C=C); NMR (CCl_4) δ 0.97 (d, *J* = 7 Hz, 3, $CHCH_3$), 2.15 (s, 3, $COCH_3$), 6.67 (t, *J* = 4.5 Hz, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 152 (20), 109 (100), 81 (63). Anal. ($C_{10}H_{16}O$) C, H.

12j: R_f 0.41 (1:9 ether–hexane); IR (TF) 6.00 (C=O), 6.12 μm (C=C); NMR (CCl_4) δ 1.00 (d, *J* = 7 Hz, 6, $CH(CH_3)_2$), 1.4–1.9 (m, 4, CH_2), 2.0–2.4 (m, 4, allylic CH_2), 3.17 (heptet, 1, $CH(CH_3)_2$), 6.75 (m, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 152 (14), 109 (100), 81 (60). Anal. ($C_9H_{14}O$) C, H.

12k: R_f 0.42 (dichloromethane); IR (TF) 6.00 (C=O), 6.10 μm (C=C); NMR (CCl_4) δ 1.2–2.1 (m, 6, CH_2), 2.22 (s, 3, $COCH_3$), 2.2–2.7 (m, 4, allylic H), 7.02 (t, *J* = 6 Hz, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 138 (66), 123 (76), 95 (100). Anal. ($C_{10}H_{16}O$) C, H.

12l: R_f 0.47 (dichloromethane); IR (TF) 6.01 (C=O), 6.13 μm (C=C); NMR (CCl_4) δ 1.00 (t, *J* = 7 Hz, 3, CH_2CH_3), 1.2–2.1 (m, 6, CH_2), 2.1–2.6 (m, 4, allylic H), 2.63 (q, *J* = 7 Hz, 2, CH_2CH_3), 7.01 (t, *J* = 6 Hz, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 152 (30), 123 (100), 95 (76). Anal. ($C_{11}H_{18}O$) C, H.

12m: R_f 0.53 (dichloromethane); IR (TF) 6.01 (C=O), 6.14 μm (C=C); NMR (CCl_4) δ 1.03 (d, *J* = 6.5 Hz, 6, $CH(CH_3)_2$), 1.2–1.9 (m, 6, CH_2), 2.1–2.6 (m, 4, allylic H), 6.98 (t, *J* = 6.5 Hz, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 166 (18), 123 (100), 95 (50). Anal. ($C_{14}H_{24}O$) C, H.

12n: R_f 0.57 (dichloromethane); IR (TF) 6.00 (C=O), 6.12 μm (C=C); NMR (CCl_4) δ 0.6–1.0 (m, 3, CH_2CH_3), 1.0–2.1 (m, 14, CH_2), 2.1–2.7 (m, 6, allylic H and $COCH_2$), 6.97 (t, *J* = 7 Hz, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 208 (18), 138 (51), 123 (100), 95 (73). Anal. ($C_{10}H_{16}O$) C, H.

12o: R_f 0.48 (dichloromethane); IR (TF) 6.01 (C=O), 6.12 μm (C=C); NMR (CCl_4) δ 1.3–1.8 (m, 8, CH_2), 2.2–2.5 (m, 4, allylic H), 2.22 (s, 3, $COCH_3$), 6.78 (t, *J* = 8 Hz, 1, vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 152 (100), 137 (73), 123 (33), 109 (98). Anal. ($C_{14}H_{24}O$) C, H.

12p: R_f 0.22 in dichloromethane; IR (TF) 6.03 (C=O), 6.33 μm (C=C); NMR ($CDCl_3$) δ 1.08 (t, *J* = Hz, 3, CH_2CH_3), 2.58 (q, *J* = 7 Hz, 2, CH_2CH_3), 3.05 and 3.35 (2 br s, 2, allylic H), 6.86 (br s, 1, vinylic H).

12q: R_f 0.59 (dichloromethane); mp 204–207 °C; IR (TF) 6.04 (C=O), 6.32 μm (C=C); NMR ($CDCl_3$) δ 0.92 (s, 3, C-18 angular CH_3), 1.04 (s, 3, C-19 angular CH_3), 1.14 (s, 9, $C(CH_3)_3$), 2.22 (s, 3, $COCH_3$), 5.43 (m, 1, C-6 vinylic H), 6.68 (m, 1, C-16 vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 370 (73), 314 (64), 258 (100). Anal. ($C_{25}H_{38}O_2$) C, H.

12r: R_f 0.46 (1:1 ether–hexane); mp 164–166 °C (lit.[71] mp 165–167 °C); IR (KBr) 6.04 (C=O), 6.32 μm (C=C); NMR (CCl_4) δ 0.88 (s, 3, C-18 angular CH_3), 1.03 (s, 3, C-19 angular CH_3), 2.16 (s, 3, $COCH_3$), 5.29 (m, 1, C-6 vinylic H), 6.57 (m, 1, C-16 vinylic H); mass spectrum (70 eV), *m/e* (relative intensity) 314 (11), 296 (32), 85 (100). Anal. ($C_{26}H_{38}O_3$) C, H.

12s: R_f 0.65 (dichloromethane); mp 189–192 °C (lit.[72] mp 193–194 °C); IR (KBr) 6.07 (C=O), 6.23 (C=C), 6.33 μm (aromatic); NMR ($CDCl_3$) δ 0.92 (s, 3, C-18 angular CH_3), 2.28 (s, 3, $COCH_3$), 3.77 (s, 3, OCH_3), 6.5–7.4 (m, 3, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 310 (100), 173 (36), 160 (23), 147 (14). Anal. ($C_{21}H_{26}O_2$) C, H.

16: IR (TF) 5.89 (C=O), 12.63 μm; ^{1}H NMR ($CDCl_3$) δ 1.04 (t, *J* = 7 Hz, 3, CH_2CH_3), 2.33 (m, 2, CH_2CH_3), 2.56 and 2.74 (2 br s, 2, 2 CH), 3.36 (br s, 1, OCH); ^{13}C NMR ($CDCl_3$) δ 7.36 (q), 23.7 (t), 25.92 (t), 30.30 (t), 37.80 (d), 37.82 (d), 58.82 (d), 63.19 (s); mass spectrum (70 eV), *m/e* (relative intensity) 166 (M^+, 2), 137 (5), 109 (25), 81 (100).

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Registry No. **1a**, 2570-96-9; **1b**, 53244-19-2; **1c**, 53154-02-2; **1d**, 33802-51-6; **1e**, 58422-60-9; **1f**, 53244-17-0; **1g**, 53097-56-6; **1h**, 54321-42-5; **1i**, 766-05-2; **1j**, 87184-40-5; **1k**, 95-11-4; **1l**, 3008-09-1; **1m**, 58462-92-3; **1n**, 62623-47-6; **1o**, 62623-54-5; **1p**, 1823-91-2; **1q**, 769-68-6; **1r**, 5558-78-1; **1s**, 5558-29-2; **1t**, 3508-98-3; **1u**, 5558-34-9; **1v**, 58422-61-0; **1w**, 6443-81-8; **1x**, 15601-30-6; **1y**, 3893-23-0; **1z**, 51965-61-8; **1aa**, 2184-88-5; **1bb**, 31007-06-4; **1cc**, 54321-43-6; **1dd**, 24168-42-1; **1ee**, 86-29-3; **1ff**, 4578-79-4; **1gg**, 7599-05-5; **2a**, 111-13-7; **2b**, 2235-83-8; **2c**, 823-76-7; **2d**, 103-79-7; **2e**, 577-16-2; **2f**, 54321-44-7; **2g**, 102-04-5; **2h**, 25870-62-6; **2i**, 108-94-1; **2i** (DNP hydrazone), 1589-62-4; **2j**, 87184-41-6; **2j** (2-ene), 4556-09-6; **2k**, 694-98-4; **2l**, 6372-63-0; **2m**, 1051-35-0; **2m** (dione), 57-83-0; **2n**, 62623-50-1; **2o**, 1624-73-3; **2p**, 98-86-2; **2q**, 93-55-0; **2r**, 495-40-9; **2s**, 611-70-1; **2t**, 1009-14-9; **2u**, 2050-07-9; **2v**, 37608-93-8; **2w**, 5407-91-0; **2x**, 6008-36-2; **2y**, 712-50-5; **2z**, 403-42-9; **2aa**, 99-91-2; **2bb**, 100-06-1; **2cc**, 92-91-1; **2dd**, 941-98-0; **2ee**, 119-61-9; **2ff**, 611-94-9; **2gg**, 1144-74-7; **4a**, 87184-42-7; **4b**, 87184-43-8; (*E*)-**4c**, 87184-44-9; (*Z*)-**4c**, 87184-57-4; **4d**, 60727-59-5; (*E*)-**4e**, 87184-45-0; (*Z*)-**4e**, 87184-56-3; **4f**, 60727-60-8; **4g**, 87184-46-1; **4h**, 4435-18-1; **4i**, 53153-78-9; **4j**, 53153-79-0; **4k**, 53153-80-3; **4l**, 60727-61-9; **4m**, 60727-62-0; **4n**, 60727-63-1; **4o**, 60727-64-2; **4p**, 87184-47-2; **4q**, 60727-73-3; **4r**, 60761-65-1; **4s**, 60727-74-4; **5a**, 2537-48-6; **5b**, 29668-61-9; **5c**, 34491-76-4; **5d**, 60755-26-2; **5e**, 60727-56-2; **7p**, 53097-53-3; **7q**, 51965-62-9; **7s**, 87184-48-3; **7x**, 87184-49-4; **7z**, 87184-50-7; **7aa**, 53174-18-8; **7dd**, 87184-51-8; **7ee**, 53097-54-4; **10p**, 54835-27-7; **10q**, 54835-28-8; **10s**, 54835-29-9; **10x**, 54835-31-3; **10y**, 54835-30-2; **10z**, 54835-33-5; **10aa**, 54835-34-6; **10bb**, 54835-35-7; **10dd**, 54835-36-8; **10ee**, 54835-32-4; **11**, 931-59-9; **12a**, 66917-82-6; **12b**, 63859-55-2; **12c**, 87184-52-9; (*E*)-**12d**, 87184-53-0; (*Z*)-**12d**, 87184-58-5; **12f**, 61058-97-7; **12g**, 87184-54-1; **12i**, 56922-88-4; **12j**, 14377-11-8; **12k**, 42827-59-8; **12l**, 60727-68-6; **12m**, 60727-69-7; **12n**, 17339-74-1; **12o**, 65938-08-1; **12p**, 71720-43-9; **12q**, 60727-75-5; **12r**, 60727-76-6; **12s**, 21321-91-5; **14**, 14845-55-7; **16**, 87184-55-2; *t*-$C_4H_9Si(CH_3)_2Cl$, 18162-48-6; Ag_2O, 20667-12-3; C_2H_5CN, 107-12-0; $Br(CH_2)_3C_6H_5$, 637-59-2; NaCN, 143-33-9; $C_6H_5(CH_2)_2CN$, 645-59-0; CH_3I, 74-88-4; 2-$CH_3C_6H_4CH_2CN$, 22364-68-7; c-C_5H_9Br, 137-43-9; $C_6H_5CH_2Cl$, 100-44-7; *n*-C_4H_9Br, 109-65-9; c-$C_6H_{11}CONH_2$, 1122-56-1; $C_6H_5CH_2CN$, 140-29-4; C_2H_5I, 75-03-6; *n*-C_3H_7Br, 106-94-5; *i*-C_3H_7Br, 75-26-3; *i*-$C_5H_{11}Br$, 107-82-4; $(CH)_3CCH_2CH_2Br$, 1647-23-0; *n*-$C_8H_{17}Br$, 111-83-1; 4-$(CH_3O)C_6H_4CH_2CN$, 104-47-2; 4-$(C_6H_5)C_6H_4CH_2CN$, 31603-77-7; 1-$C_{10}H_7CH_2CN$, 132-75-2; *i*-C_3H_7CHO, 78-84-2; *n*-$C_6H_{13}CHO$, 111-71-7; $C_6H_5(CH_2)_2COCH_3$, 2550-26-7; $(n\text{-}C_4H_9)_2CO$, 502-56-7; *i*-$C_3H_7COC_6H_5$, 611-70-1; $P(OC_2H_5)_3$, 122-52-1; 2-bromooctane, 557-35-7; 2-cyclohexylidene propionitrile, 53153-76-7; 1-phenyl-1,3-butadiene, 1515-78-2; acrylonitrile, 107-13-1; cyclopentadiene, 542-92-7; anthracene, 120-12-7; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; cyclododecanone, 830-13-7; norcamphor, 497-38-1; butyric acid, 107-92-6; 2-bromobutyramide, 5398-24-3; 2-bromobutyronitrile, 41929-78-6; 3-methylbutyric acid, 503-74-2; 2-bromo-3-methylbutyramide, 7472-46-0; 2-bromo-3-methylbutyronitrile, 25117-57-1; octanoic acid, 124-07-2; 2-bromooctanamide, 15364-13-3; 2-bromooctanenitrile, 51201-57-1.