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On the Preparation of Acyl Cyanides from Aldehydes

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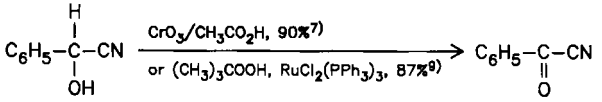
The *O*-silylated cyanohydrins **3** prepared from the aldehydes **1** with trimethylsilyl cyanide are oxidized photochemically or thermally with *N*-bromosuccinimide to afford the acyl cyanides **4a–n**. Scope and limitations of the procedure are discussed.

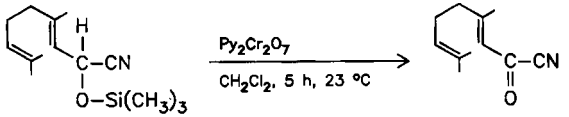
Zur Darstellung von Acylcyaniden aus Aldehyden

Die aus den Aldehyden **1** mit Trimethylsilylcyanid dargestellten *O*-silylierten Cyanhydrine **3** werden photochemisch oder thermisch mit *N*-Bromsuccinimid zu den Acylcyaniden **4a–n** oxidiert. Es werden Grenzen und Möglichkeiten des Verfahrens beschrieben.

Acyl cyanides are typically prepared by the reaction of acyl halides with various metallic cyanides or trimethylsilyl cyanide[1–6]. In some cases aldehydes instead of acyl halides were used as starting materials. Thus, cyanohydrins of aromatic aldehydes can be oxidized to acyl cyanides with CrO_3/CH_3CO_2H[7] or, more recently, ruthenium catalyzed with *tert*-butyl hydroperoxide[8,9], e. g.

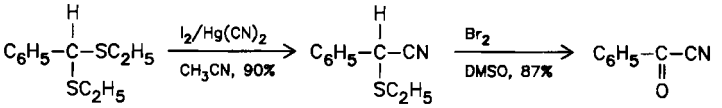


Bromine[10] or manganese dioxide[11] have also been tried as oxidizing agents. *Corey* et al.[12] dehydrogenated *O*-silylated cyanohydrins of α,β-unsaturated aldehydes to acyl cyanides with pyridinium dichromate in methylene chloride and state that this oxidation is not generally efficient and cannot be extended satisfactorily to nonconjugated aldehydes[13].



58% *E*,*Z*-mixture

Acyl cyanides can be obtained from dithioacetals of aromatic aldehydes *via* α-alkylthio nitriles[14], e. g.



and by special methods[15–17].

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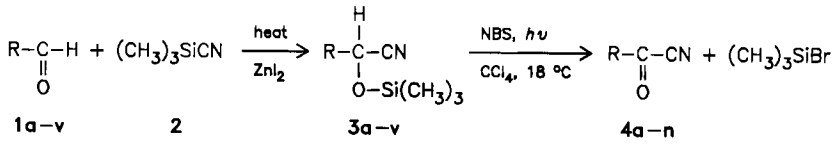
In this communication we would like to report that the *Wohl-Ziegler* oxidation[18,19] with *N*-bromosuccinimide (NBS) can be satisfactorily used to dehydrogenate *O*-silylated cyanohydrins of both aliphatic and aromatic aldehydes to acyl cyanides (Table 1, 2).



The *O*-silyl cyanohydrins **3** are easily prepared following the procedure of *Evans* et al.[20–22] and recent improvements[23–27] (Table 1). Since trimethylsilyl cyanide is now readily available[28–30] and since the stable protected cyanohydrins **3** are formed irreversibly the use of **3** instead of unprotected cyanohydrins for the preparation of acyl cyanides **4** has advantages. The NBS oxidation of compounds **3** can be carried out either thermally in boiling carbon tetrachloride or, better, photochemically in the same solvent at room temperature (18 °C) requiring typical reaction times in the order of a few minutes.

Scope and limitations (Table 2) are comparable to other *Wohl-Ziegler* oxidations. Thus, the complete separation of succinimide can cause problems (e.g. in the case of **4i**). Separation problems arise when the acyl cyanide and trimethylsilyl bromide (b.p. 79 °C) or the solvent have similar boiling points, e.g. **3o, p** reacted with NBS, but the acyl cyanides could not be obtained pure. The forming trimethylsilyl bromide may react with the acyl cyanide, for instance in the case of **3q**. Attempts to circumvent this problem by running the reaction in the presence of one equivalent of trimethyl orthoformate[31,32] proved to be unsuccessful. The NBS oxidation procedure cannot be applied to cyanohydrins, which contain other oxidizable functional groups. The aldehyde **3r**, for instance, reacted with NBS preferently at the aldehydic group, and the olefin **3s** undergoes allylic bromination giving rise to a mixture of *O*-silylated cyanohydrins, while the corresponding saturated cyanohydrin **3d** can be oxidized to **4d** without problems. The unsaturated cyanohydrins **3u, v** were recovered unchanged after 72 respectively 47 hours of irradiation in the presence of NBS. The crotonaldehyde derivative **3t**, on the other hand, reacted completely within 20 min. The resulting mixture of compounds showed strong absorptions at 2200 (CN) and 1680 (CO) cm^{-1}, indicating the presence of an acyl cyanide. In the ^1H NMR spectra strong *O*-trimethylsilyl signals were still observed suggesting that in part allylic bromination of the methyl group had occurred. In consequence, α,β-unsaturated acyl cyanides cannot be prepared satisfactorily by the NBS procedure.

From the other oxidizing agents examined bromine may be suitable in certain cases. Irradiation of a solution of **3f** in the presence of one equivalent of bromine resulted in the isolation of especially pure **4f**. This compound was also obtained with *N*-bromophthalimide as oxidizing agent, while *N*-chlorosuccinimide, trichloroisocyanuric acid, sulfuryl chloride or chloramine-T were unreactive. With

Table 1. Physical Data of the Cyanohydrins **3a–v**

3	R Yield [%]; b.p. [°C/torr][a]	^{1}H NMR[b]	^{13}C NMR[b]
a	$CH_3[CH_2]_4$[20] 66; 106/20[24]	CH_3 0.22, 0.90 (m), CH 4.41 (t, J = 6.6 Hz)[c]	CH_3 −0.4, 14.0, CH_2 22.5, 24.2, 31.1, 36.0, CH 61.3, CN 120.1[c]
b	$(C_2H_5)_2CH$ 82; 82–84/13[25]	CH_3 0.21, 0.94 (t, J = 7 Hz), HCO 4.41 (d, J = 4.3 Hz)	CH_3 −0.4, 11.2, 11.4, CH_2 21.7, 21.8, CH 46.6, 64.2, CN 119.6
c	$(CH_3)_2CHCH_2$[24] 94; 69/13[25]	CH_3 0.21, 0.94 (d, J = 7 Hz), 0.96 (d, J = 7 Hz), HCO 4.44 (q, J = 6 and 7 Hz)	CH_3 −0.3, 22.0, 22.5, CH_2 24.3, CH 45.2, 60.1, CN 120
d	$(CH_3)_2CH[CH_2]_3CH(CH_3)CH_2$ 91; 73–78/0.1[25][d]	CH_3 0.21, 0.87 (d, J = 7 Hz, 2 CH_3), 0.93 (d, J = 7 Hz), OCH 4.46 (m)	CH_3, CH_2, CH −0.3, 19.1, 19.7, 22.5, 22.6, 24.4, 27.9, 28.8, 29.1, 36.8, 37.1, 39.2, 43.5, OCH 59.8, 60.3, CN 120.1, 120.3
e	$C_6H_5CH_2$ 86; 83–85/0.1[25]	CH_3 0.07, CH_2 3.03 (d, J = 7 Hz), OCH 4.48 (t, J = 7 Hz)	CH_3 −0.6, CH_2 42.7, CH 62.8, CN 119.4, *i,p*-C 127.3, 134.9, *o,m*-C 128.4, 129.6
f	C_6H_5[20,23,24,26]	OCH 5.49	OCH 63.4, CN 119.1, *i,p*-C 129.2, 135.9, *o,m*-C 126.2, 128.8
g	4-Cl-C_6H_4[23,25] 70; 84–85/0.1[24]	CH_3 0.23, OCH 5.50[c,e]	CH_3 −0.4, CH 62.7, CN 118.8, *i,p*-C 134.5, 134.9, *o,m*-C 127.5, 128.9[c]
h	2-$CH_3C_6H_4$ 94; 73–75/0.1[25]	CH_3 0.21, 2.42, OCH 5.56[e]	CH_3 −0.2, 18.7, CH 62.1, CN 118.7, C-1,2 134.2, 135.6, C-3,4,5,6 126.4, 127.0, 129.3, 131.0
i	4-$NO_2C_6H_4$[26]		CH 62.8, CN 118.2, *i,p*-C 143.1, 148.5, *o,m*-C 124.0, 127.1
j	4-$CH_3OC_6H_4$[23,25]	CH_3 0.20, 3.79, OCH_3 5.43[e]	CH_3 −0.2, 55.3, CH 63.4, CN 119.2, *i*-C 128.6, *p*-C 160.4, *o*-C 114.3, *m*-C 127.8
k	4-$(CH_3)_3SiOC_6H_4$ 59; 97–102/0.1[25][f]	CH_3 0.20, 0.27, OCH 5.44, CH 6.87 (d, J = 8.6 Hz), 7.35 (d, J = 8.6 Hz)[c]	CH_3 −0.3, 0.1, OCH 63.2, CN 119.3, *i*-C 129.0, *p*-C 155.8, *o*-C 120.3, *m*-C 127.8[c]
l	4-NCCH[OSi$(CH_3)_3$]C_6H_4[26] 76; 146–148/0.1[25]	CH_3 0.24, OCH 5.53, CH 7.53	CH_3 −0.3, OCH 63.2, CN 118.9, CH 126.8, C 137.6
m	3-thienyl 82; 82–85/0.1[24]	CH_3 0.21, OCH 5.57[c,e]	CH_3 −0.3, OCH 59.5, CN 118.7, C-3 136.7, CH 123.6, 125.4, 127.3[c]
n	2-pyridyl[26] 92; 104–105/0.1[25]	CH_3 0.27, OCH 5.62	CH_3 −0.31, OCH 65.2, CN 118.6, CH, C 120.4, 123.9, 137.3, 149.3, 155.5

Table 1 (*Continued*)

3	R Yield [%]; b.p.[°C/torr][a]	^{1}H NMR[b]	^{13}C NMR[b]
o	$(CH_3)_3C$ 40; 106/68[25]	CH_3 0.21, 1.01, CH 3.99	CH_3 0.0, 25.4, C 36.3, CH 71.4, CN 119.6
p	Cl_3C 70; 90–92/13[25][f]	CH_3 0.33, CH 4.89	CH_3 −0.3, CH 74.9, CCl_3 96.6, CN 114.9
q	$\overline{CH_2OC(CH_3)_2OCH}$ 70; 105–106/13[25][f]	CH_3 0.22, 0.24, 1.36 (2 CH_3), 1.46, 1.50	CH_3 −0.3, −0.4, 24.9 (2 CH_3), 26.2, 26.7, CH_2, CH 62.9, 63.5, 65.7, 75.9, 76.4, OCO 110.6, 110.7, CN 117.8, 118.4
r	4-$OHCC_6H_4$ 26; 117–122/0.1[25]	CH_3 0.28, OCH 5.68, 10.05, CH 7.69 (d, J = 8.2 Hz), 7.95 (d, J = 8.2 Hz)[c]	CH_3 −0.4, OCH 62.9, 191.6, CN 118.5, *i,p*-C 136.5, 142.1, *o,m*-C 126.7, 130.1[c]
s	$(CH_3)_2C{=}CH[CH_2]_2CH(CH_3)CH_2$ 34; 70–74/0.1[25][d]	CH_3 0.22, 0.91 (d, J = 7 Hz), 0.95 (d, J = 7 Hz), 1.61, 1.69, CH 4.46 (m), 5.08 (m)[c]	$SiCH_3$ −0.5, CH_3, CH_2 17.6, 18.6, 19.5, 25.0, 25.1, 25.7, 28.0, 28.3, 36.2, 36.8, 43.0, OCH 59.3, 59.8, CN 120.1, 120.3, =C 123.8, 123.9, 131.4, 131.5[c]
t	$CH_3CH{=}CH$[20,24,27]	CH_3 0.21, 1.76 (d, J = 6.7 Hz), HCO 4.89 (d, J = 6.1 Hz), CH 5.55 (m), 5.96 (m)	CH_3 −0.1, 17.3, HCO 62.2, CN 118.6, =C 126.5, 130.9
u	$C_6H_5CH{=}CH$[20,24,27]	CH_3 0.25, OCH 5.10 (q, J = 1.3 and 6.1 Hz), CH 6.19 (q, J = 6.1 and 15.9 Hz), 6.79 (d, J = 15.9 Hz)[c]	CH_3 −0.2, OCH 62.1, CN 118.3[c]
v	$C_6H_5C{\equiv}C$ 55; 115–117/0.1[25]	CH_3 0.29, CH 5.47	CH_3 −0.1, HCO 51.9, C 81.4, 86.9, CN 116.1, *i,p*-C 120.6, 129.3, *o,m*-C 128.3, 131.6

[a] Yields of analytically pure compounds, typically after two distillations through a 30-cm Vigreux column. The compounds were prepared according to the procedure as given in the reference. – [b] Bruker WM-250 spectrometer; internal reference tetramethylsilane; δ-scale; temperature 303 K. – [c] At 263 K. – [d] Compound **3d**: 4(*R*)-form; $\alpha_D^{23} = -0.32°$ (pure, 1-dm tube). Compound **3s**: 4(*R*)-isomer; $\alpha_D^{23} = -0.28°$ (pure, 1-dm tube). – [e] IR (film): Compound **3g**: 2230 cm^{-1}; **3h**: 2230; **3j**: 2220 cm^{-1}; **3m**: 2230 cm^{-1}; **3v**: 2220 cm^{-1}. For the other compounds a CN absorption was not observed. – [f] Prepared according to ref.[25] but without catalyst.

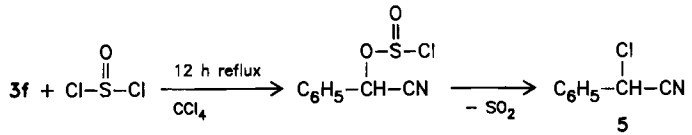
Table 2. Physical Data of the Acyl Cyanides **4a–n**

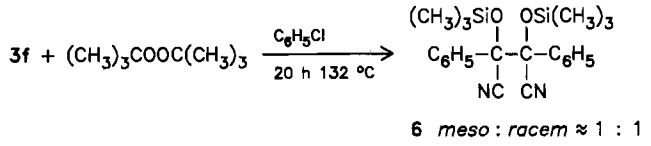
4[a]	Yield[b]; b.p. [%]; [°C/torr]	IR (CCl_4) [cm^{-1}]	^1H NMR[c]	^{13}C NMR[c]
a	71; 115–116/103	2200, 1720	CH_3 0.92 (t, J = 7 Hz), CH_2CO 2.74 (t, J = 7 Hz)	CH_3, CH_2 13.7, 22.2, 22.6, 30.8, 45.0, CN 113.3, CO 177.0
b	66; 84–87/75	2200, 1710	CH_3 0.95 (t, J = 7 Hz), CH 2.50 (m)	CH_3 11.2, CH_2 22.6, CH 56.8, CN 112.8, CO 180.7
c[41]	51; 69–73/72	2200, 1715	CH_3 1.01 (d, J = 7.7 Hz), CH 2.33 (m), CH_2 2.65 (d, J = 7.0 Hz)[d]	CH_3, CH_2 22.1, 24.3, CH 53.4, CN 113.3, CO 176.8[d]
d[e]	83; 50–55/0.1	2200, 1720	CH_3 0.88 (d, J = 6.7 Hz, 2 CH_3), 0.99 (d, J = 6.7 Hz), CH_2CO 2.54 (q, J = 7.9 and 16.5 Hz), 2.72 (q, J = 6.1 and 16.5 Hz)	CH_3, CH_2, CH 19.5, 22.5, 22.6, 24.5, 27.9, 29.3, 36.8, 38.9, 52.2, CN 113.4, CO 176.7
e[6]	61; 102–104/13	2200, 1720	CH_2 3.93	CH_2 51.1, CN 112.9, CO 173.9
f[3]	82; 88/13	2200, 1680		CN 112.6, CO 167.7
g[3,17]	93; 42–44[f]	2200, 1680	CH 7.62 (d, J = 8.5 Hz), 8.12 (d, J = 8.5 Hz)[d]	CN 112.3, CO 166.5, *i,p*-C 131.4, 143.8, *o,m*-C 129.9, 131.5[d]
h[3]	49; 102–103/13	2200, 1680	CH_3 2.62[d]	CH_3 22.2, CN 113.2, CO 168.3, CH 126.7, 130.9, 132.7, 135.0, 135.7, 142.7[d]
i[42]	47; 108–113[f]	2210, 1690		CN 112.0, CO 166.3, *i*-C 137.0, *p*-C 152.2, *o,m*-C 124.6, 131.4
j[3]	91; 58–60[f]	2200, 1670	CH_3 3.97, CH 7.07 (d, J = 8.8 Hz), 8.12 (d, J = 8.8 Hz)[d]	CH_3 56.0, CN 112.9, CO 166.4, *i*-C 126.3, *o*-C 133.1, *m*-C 114.8, *p*-C 165.8[d]
k	76; 75–77/0.1	2200, 1670	CH_3 0.37, CH 7.01 (d, J = 8.6 Hz), 8.08 (d, J = 8.6 Hz)[d]	CH_3 0.5, CN 113.1, CO 166.2, *p*-C 163.6, *i,o,m*-C 120.9, 127.0, 133.3[d]
l[43]	83; 143–146[f]	2210, 1680	CH 8.40	CN 112.1, CO 166.7, C-1,4 138.3, C-2,3,5,6 130.9
m	86; 43–44[f]	2210, 1670		CN 113.1, CO 160.2, CH 126.2, 128.6, 139.6
n	42; 54–56[f]	2210, 1700		CN 113.5, CO 169.1, C-2 149.8, CH 123.8, 129.7, 137.6, 150.6

[a] R as in Table 1. – [b] Yields of isolated analytically pure compounds. – [c] See footnote[b] in Table 1. – [d] At 263 K. – [e] α_D^{23} = +10.42 (pure, 1-dm tube). – [f] m.p. [°C].

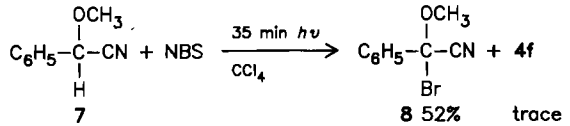
thionyl chloride **3f** gave chlorophenylacetonitrile (**5**). A similar reaction is known for the unprotected cyanohydrin[33].

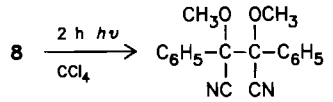
Oxidation of **3f** with di-*tert*-butylperoxide in boiling chlorobenzene gave the dimer **6**[34] as a 1:1-mixture of the *meso* and *racem* form.





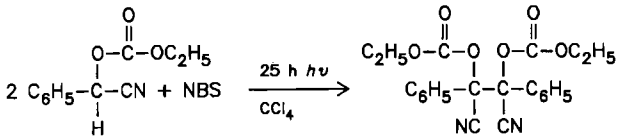
6 *meso* : *racem* ≈ 1 : 1

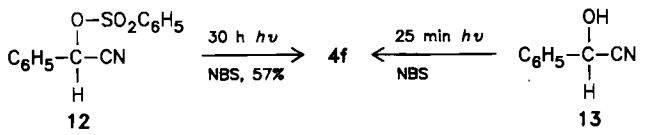


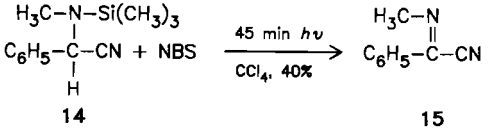


9 61%, *meso* : *racem* ≈ 1 : 1

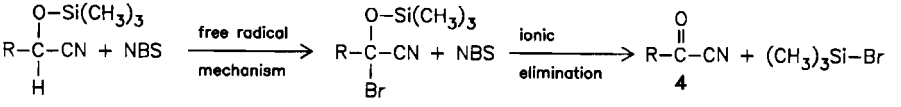
Varying the *O*-protective group we found that the *O*-methyl compound **7** was readily brominated photochemically with NBS to give **8** besides small amounts of **4f** and **9**. The latter compound arises from irradiation of **8**. The oxidation of **7** with bromine led to mixtures of compounds. Recently, *Rüchardt* et al.[35] oxidized **8** with di-*tert*-butylperoxide to obtain **9**. The *O*-acylated cyanohydrin **10** was slowly oxidized photochemically with NBS to give **11** in low yield. The *O*-sulfonyl compound **12**[35] gave **4f** in a rather slow reaction. The acyl cyanide **4f** was also obtained by NBS oxidation of the unprotected cyanohydrin **13**.



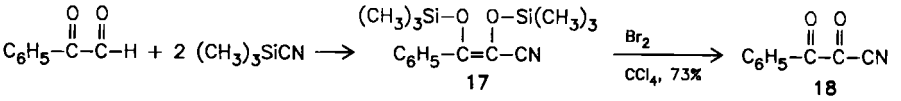




14 15



16 4



17 18

Finally, photochemical NBS oxidation of the silylated aminonitrile **14**[36] resulted in the formation of the iminonitrile **15**[37] in moderate yields.

All these photochemical brominations with NBS follows most likely a free-radical *Goldfinger* mechanism[38,39] leading to an intermediate, e.g. **16**, which eliminates trimethylsilyl bromide. Recently, *Rüchardt* et al.[35] published a thorough investigation on thermodynamic and kinetic aspects of the radical derived from **7** by H abstraction. A capto-dative stabilization[40] of the radical has not been found in this case. That the transformation **16** to **4** does not require light can be seen, for instance, from the reaction of **17** with bromine, which proceeds readily in the dark giving the oxoacyl cyanide **18**.

We would like to thank Mr. *S. Herzberger* for technical assistance.

Experimental Part

IR: Perkin-Elmer IR 299. Photoreactor: 13/12 DEMA (H. Mangels) with a Philips high-pressure lamp HPK 125. All reactions were carried out with exclusion of moisture in absolute solvents. Melting points: uncorrected.

2-(Trimethylsiloxy)heptanenitrile (**3a**)[20]: A suspension of dried powdered sodium iodide (10 g), dried powdered potassium cyanide (29.30 g, 450 mmol), trimethylsilyl chloride (48.89 g, 450 mmol), and pyridine (10 ml) in acetonitrile (220 ml) was stirred under nitrogen at 23°C for ca. 24 h until the signal for trimethylsilyl chloride in the ^{1}H NMR spectrum had completely disappeared[24]. Hexanal (40.06 g, 400 mmol) was added dropwise in the course of 30 min, and the reaction mixture was stirred until the carbonyl band in the IR spectrum had disappeared (ca. 2 h). Addition of pentane (300 ml), pouring into ice water (1000 ml), separation of the organic layer and extraction of the aqueous layer several times with pentane, washing the combined organic layers with cold (0°C) sodium hydrogensulfite solution, drying over sodium sulfate, and evaporation of the solvent left an oily residue. Fractionating distillation afforded a colourless oil (58.97 g, 66%); b.p. 106°C/20 torr.

3-Ethyl-2-(trimethylsiloxy)pentanenitrile (**3b**): 2-Ethyl-butanol (53.86 g, 400 mmol) was added dropwise at 23°C to a mixture of trimethylsilyl cyanide (43.65 g, 440 mmol) and anhydrous zinc iodide (ca. 0.5 g). The mixture was heated to 90–100°C until the carbonyl absorption in the IR spectrum had disappeared (ca. 3 h)[25]. Distillation afforded a colourless oil (65.39 g, 82%); b.p. 82–84°C/13 torr.

$C_{10}H_{21}NOSi$ (199.4) Calcd. C 60.24 H 10.62 N 7.03 Found C 59.99 H 10.51 N 7.17

4-Methyl-2-(trimethylsiloxy)pentanenitrile (**3c**)[24]: From 3-methylbutanal (43.07 g, 500 mmol). After 2 h at 80°C the reaction was completed. Pale yellow oil.

4(R),8-Dimethyl-2-(trimethylsiloxy)nonanenitrile (**3d**): From dihydrocitronellal (31.25 g, 200 mmol). Before distillation ca. 0.1 g of copper powder was added to bind iodine. Colourless oil.

$C_{14}H_{29}NOSi$ (255.5) Calcd. C 65.82 H 11.44 N 5.48 Found C 65.93 H 11.28 N 5.51

3-Phenyl-2-(trimethylsiloxy)propanenitrile (**3e**): From phenylacetaldehyde (36.04 g, 300 mmol). The sideproduct 2-phenyl-1-(trimethylsiloxy)ethen (ca. 5%) could be separated by distillation over a 40-cm Vigreux column. Colourless oil.

$C_{12}H_{17}NOSi$ (219.4) Calcd. C 65.70 H 7.81 N 6.39 Found C 65.87 H 7.71 N 6.65

Phenyl(trimethylsiloxy)acetonitrile (**3f**)[20,23,24,26]: Preparation according to ref.[25].

(4-Chlorphenyl)(trimethylsiloxy)acetonitrile (**3g**)[23,25]: From 4-chlorobenzaldehyde (56.23 g, 400 mmol). Colourless oil.

(2-Methylphenyl)(trimethylsiloxy)acetonitrile (**3h**): From 2-methylbenzaldehyde (36.04 g, 300 mmol). Reaction time 45 min. Distillation with added copper powder afforded a colourless oil.

$C_{12}H_{17}NOSi$ (219.4) Calcd. C 65.70 H 7.81 N 6.39 Found C 65.77 H 7.75 N 6.51

(4-Nitrophenyl)(trimethylsiloxy)acetonitrile (**3i**)[26]: Prepared as described in ref.[26].

(4-Methoxyphenyl)(trimethylsiloxy)acetonitrile (**3j**)[23,25]: Prepared as described in ref.[25].

(Trimethylsiloxy)[(4-trimethylsiloxy)phenyl]acetonitrile (**3k**): A mixture of 4-hydroxybenzaldehyde (48.85 g, 400 mmol) and trimethylsilyl chloride (65.19 g, 600 mmol) was boiled under reflux for 20 h. After cooling to 23°C trimethylsilyl cyanide (47.62 g, 480 mmol) was added dropwise. Stirring for 20 h at 90°C and distillation afforded a colourless oil, which was redistilled.

$C_{14}H_{23}NO_2Si_2$ (293.5) Calcd. C 57.29 H 7.90 N 4.77 Found C 57.07 H 7.90 N 4.79

(1,4-Phenylene)bis[(trimethylsiloxy)acetonitrile] (**3l**)[26]: Preparation according to ref.[26]. Colourless oil.

(3-Thienyl)(trimethylsiloxy)acetonitrile (**3m**): From 3-thiophenecarbaldehyde (44.86 g, 400 mmol). Reaction time 5 h. Colourless oil.

$C_9H_{13}NOSSi$ (211.4) Calcd. C 51.14 H 6.20 N 6.63 Found C 51.44 H 6.17 N 6.75

(2-Pyridyl)(trimethylsiloxy)acetonitrile (**3n**)[26]: From 2-pyridinecarbaldehyde (21.42 g, 200 mmol). Reaction time 1 h. Colourless oil.

3,3-Dimethyl-2-(trimethylsiloxy)butanenitrile (**3o**): From pivalaldehyde (34.45 g, 400 mmol). Reaction time 7 h at 90°C. Colourless oil.

$C_9H_{19}NOSi$ (185.3) Calcd. C 58.32 H 10.33 N 7.56 Found C 58.50 H 10.56 N 7.45

3,3,3-Trichloro-2-(trimethylsiloxy)propanenitrile (**3p**): From anhydrous trichloroacetaldehyde (73.69 g, 500 mmol) without ZnI_2 as catalyst. Reaction time 8 h at 90°C. Colourless oil.

$C_6H_{10}Cl_3NOSi$ (246.6) Calcd. C 29.22 H 4.09 N 5.68 Found C 29.35 H 4.00 N 5.73

(2,2-Dimethyl-1,3-dioxolan-4-yl)(trimethylsiloxy)acetonitrile (**3q**): From (2,2-dimethyl-1,3-dioxolan)-4-carbaldehyde (6.55 g, 66 mmol) without catalyst. Reaction time 10 h at 90°C. Colourless oil.

$C_{10}H_{19}NO_3Si$ (229.4) Calcd. C 52.37 H 8.35 N 6.11 Found C 52.63 H 8.26 N 6.14

(4-Formylphenyl)(trimethylsiloxy)acetonitrile (**3r**): From terephthalaldehyde (40.24 g, 300 mmol). Reaction time 90 min at 90°C. Colourless oil.

$C_{12}H_{15}NO_2Si$ (233.3) Calcd. C 61.77 H 6.48 N 6.00 Found C 61.83 H 6.54 N 6.17

4(R),8-Dimethyl-2-(trimethylsiloxy)non-7-enenitrile (**3s**): From citronellal (61.70 g, 400 mmol). Reaction time 8 h at 90°C. Colourless oil.

$C_{14}H_{27}NOSi$ (253.5) Calcd. C 66.34 H 10.74 N 5.53 Found C 66.19 H 10.74 N 5.79

2-(Trimethylsiloxy)pent-3-enenitrile (**3t**)[20,24,27]: Preparation according to ref.[24].

(E)4-Phenyl-2-(trimethylsiloxy)but-3-enenitrile (**3u**)[20,24,27]: Preparation according to ref.[24].

4-Phenyl-2-(trimethylsiloxy)but-3-ynenitrile (**3v**): From phenylpropynal (26.03 g, 200 mmol). Reaction time 24 h at 90°C. Yellowish oil.

$C_{13}H_{15}NOSi$ (229.4) Calcd. C 68.08 H 6.59 N 6.11 Found C 68.04 H 6.56 N 6.35

Hexanoyl Cyanide (**4a**): A suspension of NBS (14.95 g, 84 mmol) and **3a** (13.96 g, 70 mmol) in carbon tetrachloride (100 ml) was irradiated with stirring under nitrogen at 18°C until in the ^1H NMR spectrum the signals of **3a** had disappeared (ca. 20 min). The reaction mixture was filtered with exclusion of moisture and the residue was three times suspended in carbon tetrachloride (20 ml) or pentane and filtered again. The combined filtrates were left for 12 h at 0°C and a small amount of succinimide was filtered off. The solvent was removed by distillation over a 40-cm Vigreux colunm and the residue was twice distilled over a 15-cm Vigreux column. Yield 6.22 g (71%) of a colourless oil; b.p. 115–116°C/103 torr.

$C_7H_{11}NO$ (125.2) Calcd. C 67.17 H 8.86 N 11.19 Found C 66.99 H 9.05 N 11.39

The other compounds **4** were prepared correspondingly.

2-Ethylbutanoyl Cyanide (**4b**): From **3b** (9.97 g, 50 mmol). Irradiation time 20 min. Colourless oil.

$C_7H_{11}NO$ (125.2) Calcd. C 67.17 H 8.86 N 11.19 Found C 66.28 H 8.84 N 10.79

3-Methylbutanoyl Cyanide (**4c**)[41]: From **3c** (9.27 g, 50 mmol). Irradiation time 30 min. Brownish oil.

3(R),7-Dimethyloctanoyl Cyanide (**4d**): From **3d** (12.78 g, 50 mmol). Irradiation time 20 min. Colourless oil.

$C_{11}H_{19}NO$ (181.3) Calcd. C 72.88 H 10.57 N 7.73 Found C 72.94 H 10.60 N 7.85

Phenylacetyl Cyanide (**4e**)[6]: From **3e** (10.97 g, 50 mmol). Irradiation time 75 min. Yellowish oil.

Benzoyl Cyanide (**4f**)[3]: a) From **3f** (12.32 g, 60 mmol) as described for **4a**. Irradiation time 25 min. The product was crystallized from carbon tetrachloride (5 ml)/pentane (5 ml) at −20°C affording pale yellow needles (5.67 g, 72%, including work-up of the mother liquor); m.p. 33–34°C (ref.[5]: 33–34°C).

b) A suspension of **3f** (14.37 g, 70 mmol) and NBS (13.71 g, 77 mmol) was stirred in pentane (75 ml) at 23°C. No reaction occurred when light was excluded. In indirect daylight the reaction rate (20 h in the instance) depended on the intensity of the light. No reaction occurred in ether as solvent. Work-up yielded a colourless oil (7.53 g, 82%); b.p. 88°C/13 torr (ref.[3]: 72–73°C/0.15 torr).

c) Under irradiation bromine (8.15 g, 51 mmol) in carbon tetrachloride (10 ml) was added dropwise to a solution of **3f** (10.27 g, 50 mmol) in carbon tetrachloride (90 ml). The reaction mixture was irradiated for further 25 min. Separation from an oily deposit and distillation

afforded a colourless oil (4.12 g, 63%; b.p. 83°C/13 torr), which soon crystallized (m.p. 32–33°C).

d) A suspension of **3f** (10.27 g, 50 mmol) and *N*-bromophthalimide (13.56 g, 60 mmol) in carbon tetrachloride (100 ml) was irradiated for 60 min at 18°C. Work-up yielded a colourless powder (4.59 g, 70%); m.p. 33–34°C.

e) As described for **4a**, but with **13** (6.66 g, 50 mmol) instead of **3f**. Irradiation time 25 min. Yield 2.82 g (43%) of a colourless oil (b.p. 84°C/13 torr), which soon crystallized (m.p. 33–34°C).

f) A suspension of **12**[35] (13.67 g, 50 mmol) and NBS (10.68 g, 60 mmol) in carbon tetrachloride (100 ml) was irradiated for 30 h at 18°C. The ^{1}H NMR spectrum still showed some starting material. Work-up afforded 3.74 g (57%) of a colourless powder; m.p. 30–31°C.

4-Chlorobenzoyl Cyanide (**4g**)[3,17]: a) From **3g** (11.99 g, 50 mmol). Irradiation time 25 min. After evaporation of the solvent the residue was dissolved in pentane (100 ml). After filtration with added charcoal the product crystallized at −20°C affording pale yellow leaflets (7.14 g, 86%, including work-up of the mother liquor); m.p. 40–41°C (ref.[17]: 40°C).

b) The reaction was carried out as described for a), but in indirect daylight at 40°C. Yield after 4 h reaction time 7.70 g (93%) of pale yellow crystals; m.p. 42–44°C.

2-Methylbenzoyl Cyanide (**4h**)[3]: From **3h** (10.97 g, 50 mmol). Irradiation time 25 min. At longer reaction times the methyl group was partly brominated. Yellowish oil.

4-Nitrobenzoyl Cyanide (**4i**)[42]: From **3i** (12.52 g, 50 mmol). Irradiation time 135 min. After evaporation of the solvent the residue was extracted in a Soxhlet apparatus with boiling pentane for 25 h. Evaporation of the pentane and recrystallization of the residue from petroleum ether (35–80°C) (1800 ml) afforded yellow prisms.

4-Methoxybenzoyl Cyanide (**4j**)[3]: From **3j** (11.77 g, 50 mmol). Irradiation time 40 min. Recrystallization from pentane (400 ml) at +20°C (work-up of the mother liquor) afforded nearly colourless needles.

4-(Trimethylsiloxy)benzoyl Cyanide (**4k**): from **3k** (5.87 g, 20 mmol). Irradiation time 15 min.

$C_{11}H_{13}NO_2Si$ (219.3) Calcd. C 60.24 H 5.98 N 6.39 Found C 60.12 H 6.03 N 6.61

Terephthaloyl Dicyanide (**4l**)[43]: From **3l** (3.33 g, 10 mmol). Irradiation time 120 min. The solvent was evaporated and the residue was taken up in dichloromethane (100 ml). Extraction with ice water (100 ml) and the usual work-up gave a solid, which was recrystallized from dichloromethane (30 ml) at −20°C to give a yellowish powder.

Thiophen-3-carbonyl Cyanide (**4m**): From **3m** (5.28 g, 25 mmol). Irradiation time 25 min. Washing the reaction mixture first with ice water (200 ml), then with 10% aqueous sodium thiosulfate and again with ice water, drying over sodium sulfate, evaporation of the solvent and twice repeated sublimation of the oily residue (60°C/13 torr) afforded colourless needles. The product soon turns yellow on light.

C_6H_3NOS (137.2) Calcd. C 52.54 H 2.21 N 10.21 Found C 52.06 H 1.93 N 10.04

Pyridine-2-carbonyl Cyanide (**4n**)[44]: From **3n** (10.32 g, 50 mmol). Irradiation time 30 min. After filtration of the reaction mixture with added charcoal and concentration to a volume of 50 ml the product crystallized at −20°C affording pale yellow needles. Recrystallization from carbon tetrachloride (25 ml)/pentane (75 ml) at +20°C gave a colourless powder.

$C_7H_4N_2O$ (132.1) Calcd. C 63.63 H 3.05 N 21.21 Found C 63.30 H 2.85 N 20.77

Chlorophenylacetonitrile (**5**)[33]: A mixture of **3f** (2.05 g, 10 mmol) and thionyl chloride (1.43 g, 12 mmol) was boiled under reflux for 18 h. Distillation afforded a colourless oil (0.64 g, 42%); b.p. 105°C/13 torr (ref.[33]: 170°C/120 torr). – ^{1}H NMR ($CDCl_3$): CH δ = 5.55.

2,3-Diphenyl-2,3-bis(trimethylsiloxy)butanedinitrile (**6**)[34]: A solution of **3f** (2.05 g, 10 mmol) and di-*tert*-butylperoxide (2.63 g, 18 mmol) in chlorobenzene (10 ml) was boiled under reflux for 20 h under nitrogen. The reaction mixture still contained ca. 20% starting material (NMR). The solvent was evaporated under reduced pressure. The semi-solid residue consisted of an equimolecular mixture of the *meso* and *racem* form (NMR). The product was dissolved in hot ether (30 min). At −20°C colourless needles (0.53 g, 26%) of one isomer crystallized; m.p. 181–183°C (ref.[34]: 187°C). – IR (CCl_4): 2220 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 263 K): CH_3 δ = −0.06. – ^{13}C NMR (CCl_4, 263 K): CH_3 δ = 0.2, C 80.8, CN 117.6, *i,p*-C 129.7, 135.8, *o,m*-C 127.4, 127.7.

The solvent of the filtrate was evaporated to a volume of 10 ml. At −20°C a colourless powder (0.18 g, 9%) crystallized consisting of a mixture of the isomers. The filtrate was evaporated and the residue was chromatographed on silica gel (10 cm × 2 cm) with pentane/ether (3:1) as eluent affording a colourless oil (0.65 g, 32%), which consisted mainly of the other stereoisomer. – IR (CCl_4): 2220 cm^{-1}. – ^{1}H NMR ($CDCl_3$): CH_3 δ = +0.23. – ^{13}C NMR ($CDCl_3$): CH_3 = 0.7, C 81.6, CN 118.8, *i,p*-C 129.4, 134.4, *o,m*-C 127.1, 127.5.

Bromomethoxyphenylacetonitrile (**8**): A solution of **7**[45] (2.94 g, 20 mmol) and NBS (4.27 g, 24 mmol) in carbon tetrachloride (50 ml) was irradiated for 35 min. Filtration, washing of the residue with pentane (2 × 15 ml), and evaporation of the solvent afforded an oil, which was dissolved in pentane (20 ml). At −20°C a small amount of succinimide crystallized, which was removed by filtration. Evaporation of the solvent and distillation of the residue afforded a yellowish oil (2.35 g, 52%); b.p. 62–64°C/0.1 torr. The first fraction of the distillation contained some **4f** and **9**. – IR (CCl_4): 2220 cm^{-1}. – ^{1}H NMR ($CDCl_3$): CH_3 δ = 3.83. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 58.2, C 83.6, CN 113.9, *i,p*-C 130.6, 137.9, *o,m*-C 125.0, 128.7.

C_9H_8BrNO (226.1) Calcd. C 47.81 H 3.57 N 6.20 Found C 48.11 H 3.61 N 6.36

2,3-Dimethoxy-2,3-diphenylbutanedinitrile (**9**)[35]: A solution of **8** (1.13 g, 5 mmol) in carbon tetrachloride (50 ml) was irradiated for 2 h. The solvent was removed i. vac. and the residue was dissolved in hot chlorobenzene (10 ml). At 0°C the almost pure *meso* form crystallized (0.20 g, 27%); m.p. 195–196°C (ref.[35]: 201–203°C). The mother liquor was evaporated under reduced pressure and the residue was dissolved in ether (10 ml). At 0°C a mixture of *meso* and *racem* form crystallized (0.11 g, 15%). The mother liquor was evaporated and the residue was dissolved in pentane (10 ml). At 0°C a yellowish powder (0.14 g, 19%) fell out consisting according to the ^{1}H NMR spectrum (CH δ = 3.48 in $CDCl_3$) to 95% of the *racem* form besides 5% of the *meso* form (CH δ = 3.37); m.p. 160–164°C (ref.[35]: 160–165°C).

(1,2-Dicyano-1,2-diphenylethylene)-bis(ethyl carbonate) (**11**): A suspension of **10**[46] (10.26 g, 50 mmol) and NBS (10.68 g, 60 mmol) in carbon tetrachloride (100 ml) was irradiated for 25 h. Washing with cold 5% sodium thiosulfate solution and with water, drying over sodium sulfate and evaporating of the solvent gave an oily mixture of compounds (NMR), which was dissolved in ether (30 ml). After filtration a colourless powder (1.76 g, 17%) crystallized at −20°C; m.p. 167–169°C after two recrystallizations from ether (50–100 ml). – ^{1}H NMR ($CDCl_3$): CH_3 δ = 1.29 (t, *J* = 7 Hz), CH_2 4.21 (q, *J* = 7 Hz). – ^{13}C NMR ($CDCl_3$): CH_3 δ = 14.0, CH_2 65.9, C 82.2, CN 113.7, C=O 150.9, *i,p*-C 129.8, 130.6, *o,m*-C 126.9, 128.2.

$C_{22}H_{20}N_2O_6$ (408.4) Calcd. C 64.70 H 4.94 N 6.86 Found C 64.52 H 4.97 N 6.83

[Methyl(trimethylsilyl)amino]phenylacetonitrile (**14**)[36]: A mixture of benzalmethylamine (17.87 g, 150 mmol), trimethylsilyl cyanide (16.37 g, 165 mmol) and zinc iodide (ca. 0.5 g) was stirred for 6 h at 5–10°C and then for 30 min at 25°C. Excess of trimethylsilyl cyanide was removed i. vac. below 40°C leaving a colourless oil (34.03 g), which could not be distilled without decomposition. – IR (film): 2220 cm^{-1}. – ^1H NMR ($CDCl_3$, 263 K): CH_3 δ = 0.22, 2.29, CH 5.27. – ^{13}C NMR ($CDCl_3$, 263 K): δ = −0.2, 29.8, CH 54.1, CN 118.4, *i,p*-C 128.2, 134.5, *o,m*-C 126.8, 128.5.

(Methylimino)phenylacetonitrile (**15**)[37]: A suspension of **14** (10.92 g, 50 mmol) and NBS (10.68 g, 60 mmol) in carbon tetrachloride (100 ml) was irradiated for 45 min. After filtration and evaporation of the solvent the residue was treated with ether (30 ml) and ice water (30 ml). The aqueous phase was extracted with ether (3 × 10 ml) and the combined ether layers were washed with ice water (10 ml), dried over sodium sulfate and evaporated under reduced pressure. Distillation of the residue afforded a colourless oil (2.88 g, 40%); b.p. 94°C/13 torr. The compound soon crystallized; m.p. 37–38°C. – IR (CCl_4): 2210, 1610 cm^{-1}. – ^1H NMR ($CDCl_3$, 263 K): CH_3 δ = 3.83. – ^{13}C NMR ($CDCl_3$, 263 K): CH_3 δ = 45.8, CN 109.3, C=N 143.1, *i,p*-C 132.0, 133.0, *o,m*-C 127.2, 128.8.

3-Phenyl-2,3-bis(trimethylsiloxy)acrylonitrile, cis,trans Mixture (**17**): As described for **3b** from phenylglyoxal (20.12 g, 150 mmol) and trimethylsilyl cyanide (32.74 g, 330 mmol) in acetonitrile (5 ml). The very exothermic reaction started after a short induction period. After 15 h at 90°C the product was distilled affording a yellow oil (35.75 g, 78%); b.p. 101–103°C/0.1 torr. – IR (film): 2190, 1610 cm^{-1}. – ^1H NMR ($CDCl_3$, 263 K): CH_3 δ = 0.14, 0.15, 0.19, 0.34. – ^{13}C NMR ($CDCl_3$, 263 K): CH_3 δ = −0.3, 0.2, 0.4, 0.6, CN, CO 111.7, 114.2, 117.0, 118.3, 151.7, 152.1.

$C_{15}H_{23}NO_2Si_2$ (305.5) Calcd. C 58.97 H 7.59 N 4.59 Found C 58.90 H 7.57 N 4.87

Phenylglyoxyloyl Cyanide (**18**): Bromine (3.20 g, 20 mmol) in carbon tetrachloride (20 ml) was added dropwise to a solution of **17** (6.11 g, 20 mmol) in carbon tetrachloride (20 ml). After 1 h at 23°C the solvent was evaporated and the residue was dissolved in carbon tetrachloride (10 ml)/pentane (15 ml). At −20°C yellow leaflets (2.32 g, 73%, including work-up of the mother liquor) crystallized; m.p. 34°C. – IR (CCl_4): 2210, 1715, 1680 cm^{-1}. – ^{13}C NMR ($CDCl_3$): CN δ = 112.5, CO 165.1, 182.1, *i*-C 130.1, *p*-C 136.2, *o,m*-C 129.3, 130.8.

$C_9H_5NO_2$ (159.1) Calcd. C 67.93 H 3.17 N 8.80 Found C 68.07 H 3.46 N 9.05

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1a: 66-25-1 / **1b**: 97-96-1 / **1c**: 590-86-3 / **1d**: 5988-91-0 / **1e**: 122-78-1 / **1g**: 104-88-1 / **1h**: 529-20-4 / **1k**: 123-08-0 / **1m**: 498-62-4 / **1n**: 1121-60-4 / **1o**: 630-19-3 / **1p**: 75-87-6 / **1q**: 5736-03-8 / **1r**: 623-27-8 / **1s**: 106-23-0 / **1v**: 2579-22-8 / **2**: 7677-24-9 / **3a**: 40326-17-8 / **3b**: 100020-20-0 / **3c**: 81758-24-9 / **3d**: 99967-26-7 / **3e**: 93554-96-2 / **3f**: 25438-37-3 / **3g**: 66985-46-4 / **3h**: 82128-96-9 / **3i**: 71189-80-5 / **3j**: 66985-48-6 / **3k**: 99967-27-8 / **3l**: 71189-81-6 / **3m**: 82069-41-8 / **3n**: 71189-77-0 / **3o**: 88522-73-0 / **3p**: 41310-00-3 / **3q**: 99967-28-9 / **3r**: 100020-21-1 / **3s**: 99967-29-0 / **3t**: 40326-20-3 / **3u**: 40326-21-4 / **3v**: 99967-30-3 / **4a**: 99967-31-4 / **4b**: 99967-32-5 / **4c**: 66582-16-9 / **4d**: 99967-33-6 / **4e**: 33472-02-5 / **4f**: 613-90-1 / **4g**: 13014-48-7 / **4h**: 5955-73-7 / **4i**: 6048-20-0 / **4j**: 14271-83-1 / **4k**: 99967-34-7 / **4l**: 99967-35-8 / **4m**: 99967-36-9 / **4n**: 87838-53-7 / **5**: 22259-83-2 / *meso*-**6**: 99967-37-0 / *rac*-**6**: 99967-38-1 / **7**: 13031-13-5 / **8**: 99967-39-2 / *meso*-**9**: 61502-56-5 / *rac*-**9**: 61502-57-6 / **10**: 6443-66-9 / **11**: 99967-40-5 / **12**: 22259-85-4 / **13**: 532-28-5 / **14**: 56249-52-6 / **15**: 21864-88-0 / (*Z*)-**17**: 99967-41-6 / (*E*)-**17**: 99967-42-7 / **18**: 5703-60-6 / ZnI_2: 10139-47-6 / benzalmethylamine: 622-29-7 / phenylglyoxal: 1074-12-0

[1] *J. Thesing, D. Witzel,* and *A. Brehm,* Angew. Chem. **68**, 425 (1956).
[2] *S. Hünig* and *R. Schaller,* Angew. Chem. **94**, 1 (1982); Angew. Chem., Int. Ed. Engl. **21**, 36 (1982).
[3] *G. A. Olah, M. Arvanaghi,* and *G. K. S. Prakash,* Synthesis **1983**, 636.
[4] *T. Ando, T. Kawate, J. Yamawaki,* and *T. Hanafusa,* Synthesis **1983**, 637.
[5] *M. Tanaka* and *M. Koyanagi,* Synthesis **1981**, 973.
[6] *H. M. R. Hoffmann, K. Haase, Z. M. Ismail, S. Preftitsi,* and *A. Weber,* Chem. Ber. **115**, 3880 (1982).
[7] *K. Kindler* and *W. Peschke,* Arch. Pharm. **269**, 581 (1931).
[8] *M. Tanaka, T. Kobayashi,* and *T. Sakakura,* Angew. Chem. **96**, 519 (1984); Angew. Chem., Int. Ed. Engl. **23**, 518 (1984).
[9] *S. Murahashi, T. Naota,* and *N. Nakajima,* Tetrahedron Lett. **1985**, 925.
[10] *J. W. Baker* and *C. K. Ingold,* J. Chem. Soc. **1929**, 423.
[11] *E. J. Corey, N. W. Gilman,* and *B. E. Ganem,* J. Am. Chem. Soc. **90**, 5616 (1968).
[12] *E. J. Corey* and *G. Schmidt,* Tetrahedron Lett. **1980**, 731.
[13] *B. S. Bal, W. E. Childers,* and *H. W. Pinnick,* Tetrahedron **37**, 2091 (1981).
[14] *F. Pochat,* Tetrahedron Lett. **1977**, 3813.
[15] *M. G. Voronkov, N. A. Keiko, T. A. Kuznetsova, V. A. Pestunovich, E. O. Tsetlina,* and *V. V. Keiko,* Zh. Obshch. Khim. **49**, 2490 (1979).
[16] *R. M. Novak,* J. Org. Chem. **28**, 1182 (1963).
[17] *M. Alajarin, P. M. Fresneda,* and *P. Molina,* Synthesis **1980**, 844.
[18] *L. Horner* and *E. H. Winkelmann,* Newer Methods of Preparative Organic Chemistry, Ed. *W. Foerst,* p. 151 ff., Academic Press, 1964.
[19] *A. Q. Hussein* and *J. C. Jochims,* Chem. Ber. **112**, 1948 (1979), and references therein.
[20] *D. A. Evans, L. K. Truesdale,* and *G. L. Carroll,* J. Chem. Soc., Chem. Commun. **1973**, 55.
[21] *D. A. Evans* and *L. K. Truesdale,* Tetrahedron Lett. **1973**, 4929.
[22] *D. A. Evans, G. L. Carroll,* and *L. K. Truesdale,* J. Org. Chem. **39**, 914 (1974).
[23] *J. K. Rasmussen* and *S. M. Heilmann,* Synthesis **1978**, 219.
[24] *F. Duboudin, Ph. Cazeau, F. Moulines,* and *O. Laporte,* Synthesis **1982**, 212.
[25] *S. Hünig* and *G. Wehner,* Chem. Ber. **113**, 324 (1980).
[26] *K. Deuchert, U. Hertenstein, S. Hünig,* and *G. Wehner,* Chem. Ber. **112**, 2045 (1979).
[27] *U. Hertenstein, S. Hünig,* and *M. Öller,* Chem. Ber. **113**, 3783 (1980).
[28] *S. Hünig* and *G. Wehner,* Synthesis **1979**, 522.
[29] *J. K. Rasmussen* and *S. M. Heilmann,* Synthesis **1979**, 523.
[30] *M. T. Reetz* and *I. Chatziiosifidis,* Synthesis **1982**, 330.
[31] *M. E. Jung* and *G. L. Hatfield,* Tetrahedron Lett. **1978**, 4483.
[32] *A. H. Schmid,* Chemiker-Ztg. **104**, 253 (1980).
[33] *B. H. Ingham,* J. Chem. Soc. **1927**, 692.
[34] *H. Neef* and *R. Müller,* J. Prakt. Chem. **315**, 367 (1973).
[35] *M. Zamkanei, J. H. Kaiser, H. Birkhofer, H.-D. Beckhaus,* and *C. Rüchardt,* Chem. Ber. **116**, 3216 (1983).
[36] *I. Ojima, S. Inaba,* and *K. Nagatsugawa,* Chem. Lett. **1975**, 331.
[37] *T. Saegusa, N. Taka-Ishi,* and *Y. Ito,* J. Org. Chem. **34**, 4040 (1969).
[38] *P. A. Gosselain, J. Adam,* and *P. Goldfinger,* Bull. Soc. Chim. Belg. **65**, 533 (1956).
[39] *J. Adam, P. A. Gosselain,* and *P. Goldfinger,* Nature (London) **171**, 704 (1953).
[40] *H.-G. Viehe, R. Merényi, L. Stella,* and *Z. Janousek,* Angew. Chem. **91**, 982 (1979); Angew. Chem., Int. Ed. Engl. **18**, 917 (1979).
[41] *W. Tschelinzeff* and *W. Schmidt,* Ber. Dtsch. Chem. Ges. **62**, 2210 (1929).
[42] *E. Zbiral* and *L. Fenz,* Monatsh. Chem. **96**, 1983 (1965).
[43] *W. R. Hertler, H. D. Hartzler, D. S. Acker,* and *R. E. Benson,* J. Am. Chem. Soc. **84**, 3387 (1962).
[44] *B. Abarca, D. J. Hayles, G. Jones,* and *D. R. Sliskovic,* J. Chem. Res. **1983**, 1341 (microfiche).
[45] *K. Utimoto, Y. Wakabayashi, T. Horiie, M. Inoue, Y. Shishiyama, M. Obayashi,* and *H. Nozaki,* Tetrahedron **39**, 967 (1983).
[46] *F. Francis* and *O. C. M. Davis,* J. Chem. Soc. **95**, 1403 (1909).

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