Multicomponent *Strecker* Reaction under High Pressure

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Dedicated to Professor *Rolf Huisgen*, 'Master of Cycloaddition', on the occasion of his 85th birthday

For the first time, uncatalyzed, high-pressure (0.6 GPa) reactions with ketones have proven to be a powerful way to perform the three-component *Strecker* synthesis of α-amino nitriles in high yields. Two types of double *Strecker* reactions were achieved, but attempts to perform triple *Strecker* reactions were unsuccessful.

1. Introduction. – The synthesis of organic chemicals has reached a high degree of skillfulness. Improved analytical and separation methods contribute to more-efficient synthetic steps. Recently, *Wender et al.* gave a definition of 'ideal synthesis' [1]. Such a synthesis should lead to the desired product in as few steps as possible, in good overall yield, and by means of environmentally compatible reagents. The synthetic variables that have to be optimized are time, costs, overall yield, simplicity of performance, safety, and environmental acceptability. Reactions in which more than two starting compounds react to form a product in such a way that the majority of the atoms of the material can be found in the product are called multicomponent reactions (MCRs) [2–4] (for most-recent examples on MCRs, see [5]). This rough definition is suitable to distinguish MCRs from traditional two-component reactions and domino reactions, in which usually only one or two starting compounds are converted. A more-sophisticated view is introduced in *Table 1*. In multistep syntheses, the temporal and preparative complexity increases in proportion to the number of steps in a first approximation. These aspects are reflected in many isolation and purification operations, such as crystallization, extraction, distillation, or chromatography. Besides the multistep sequential synthesis of a target molecule, the desired product can often also be obtained

Table 1. *Basic Types of Multicomponent Reactions*

Type	General reaction scheme
I	$A + B \rightleftharpoons C \rightleftharpoons \ldots O \rightleftharpoons P$
II	$A + B \rightleftharpoons C \rightleftharpoons D \ldots O \rightarrow P$
III	$A \rightarrow B + C \rightarrow D \rightarrow \ldots O \rightarrow P$

in one-pot reactions of three or more starting compounds. Therefore, MCRs are very efficient in organic synthesis, and have represented a rapid upsurge in the literature.

The increasing interest in MCRs is best illustrated by the number of articles per year on the topic (*Fig. 1*). MCRs in which starting compounds, intermediates, and products are in a mobile equilibrium are classified as type-I reactions (*Table 1*). As different states of balance can prevail, yields between 0 and 100% are possible. In most cases, the products occur as mixtures with intermediates and starting materials, and are difficult to isolate. As the reaction often is incomplete, side reactions may lead to further impurities.

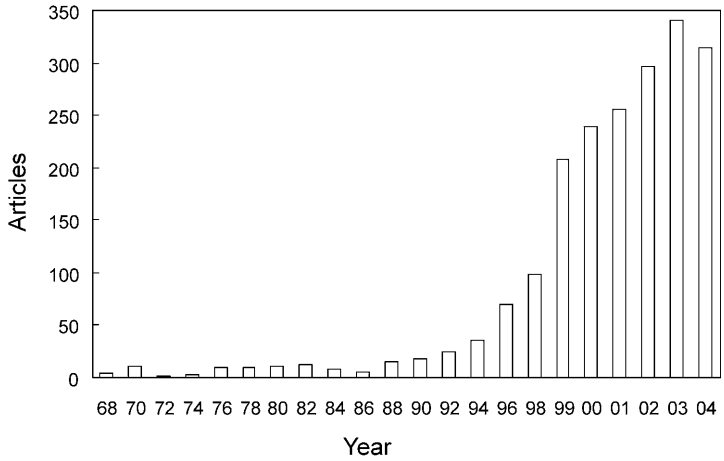


Fig. 1. *Number of publications on multicomponent reactions between 1967 and 2004*

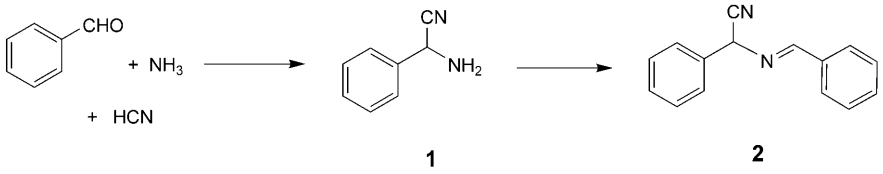
MCRs whose elementary reactions are reversible or partially irreversible, and whose last reaction step is irreversible, are type-II processes. Reactions of this type are preparatively advantageous, as the total equilibrium is shifted to the side of the products by the last irreversible step. Such irreversible steps are, *e.g.*, the result of strongly exothermic reactions such as the conversion of isocyanides, ring-closure reactions, or aromatizations.

MCRs of type III are sequences of irreversible elementary reactions. They seldom occur in preparative chemistry. Biochemical reactions in the living world typically fall into this category. Many of these reactions are *de facto* irreversible partial reactions, due either to the thermodynamic circumstances or to the combination of endothermal with exothermal processes. These reactions correspond to enzymatically accelerated and mostly highly selective reactions, so that significant amounts of side products are rarely formed. Should this, nevertheless, be the case, the side products are eliminated enzymatically and returned to the circuit. It must be considered in the above classification that these are idealizations. Many reactions cannot be assigned to one of the classes, rather the transitions are fluid.

In the following, the history and historical development of MCRs over the last 150 years are outlined. The *Strecker* synthesis of α-amino acids *via* α-amino nitriles was first published in 1850; it is generally considered to be the first MCR. However, in the

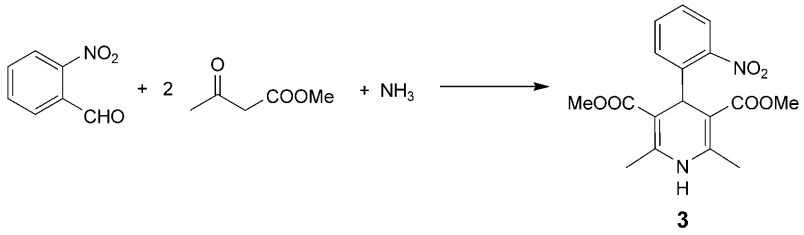
reaction of bitter almond oil and ammonia, twelve years earlier, *Laurent* and *Gerhardt* isolated a poorly soluble product that had evolved in an MCR. In this reaction (*Scheme 1*), benzaldehyde, HCN, and NH_3 first react to the amino nitrile **1**, which then reacts with a second equivalent of benzaldehyde to give the *Schiff* base **2**.

Scheme 1. *Classical* Strecker *Reaction*



Important heterocyclic compounds were first synthesized by *Radziszewski* and *Hantzsch* more than 100 years ago in a MCR. Particularly, *Hantzsch* synthesized 1,4-dihydropyridines such as **3** from NH_3, aldehydes, and 3-oxobutanoates (*Scheme 2*). A very powerful dihydropyridine derivative (nifedipine) for the therapy of cardiovascular disease was developed at *Bayer*, based on the *Hantzsch* synthesis. Also, *Mannich* and *Ugi* type reactions proved to be extremely valuable for the total synthesis of natural products. Some more-important MCRs are listed in *Table 2*.

Scheme 2. Hantzsch *Synthesis of 1,4-Dihydropyridine*



Sequential double reactions are characterized by their great elegance, frequently high stereoselectivity, and the simple manner in which they may be carried out. They permit complex molecules to be constructed in one-pot or only a few steps [6–8]. For example, *Scheiber* and *Nemes* [9] synthesized the tricyclic diamino ketone from octahydro-2*H*-quinolizin-2-one by a double *Mannich* condensation (*Scheme 3*). *Ihara and Fukumoto* [10] examined the intramolecular double *Michael* reaction by using several bases (*Scheme 4*).

Scheme 3. *Double* Mannich *Reaction*

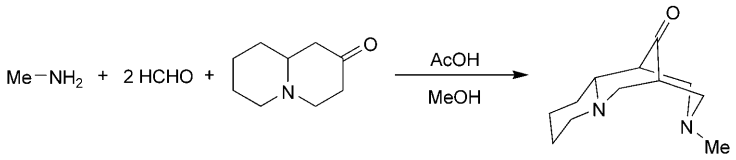
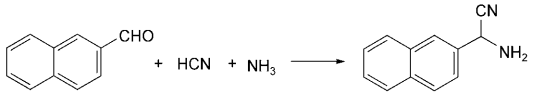
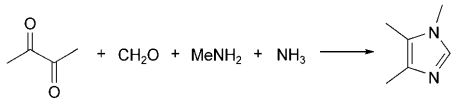
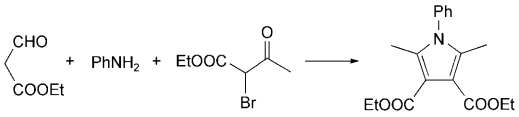
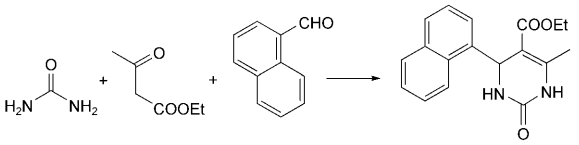
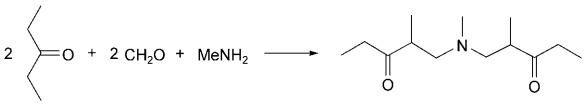
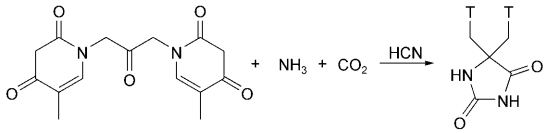
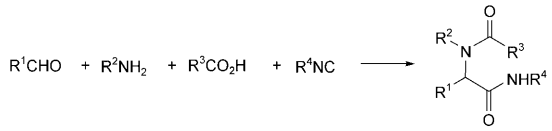


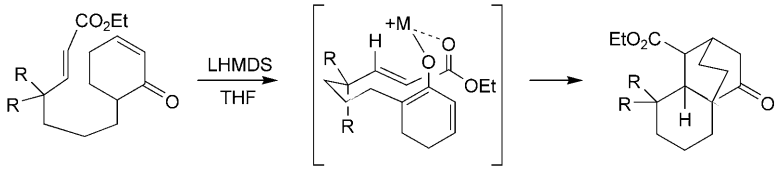
Table 2. *Historically Significant Multicomponent Reactions*

Name	Discovery	Example
Strecker synthesis	1850	
Radziszewski imidazole synthesis	1882	
Hantzsch pyrrole synthesis	1890	
Biginelli reaction	1891	
Mannich reaction	1912	
Bucherer–Bergs hydantoin synthesis[a])	1941	
Ugi reaction	1959	

[a]) T = Thymine

The development of this type of synthetic method can lead to a reduction in the amount of undesired by-products, thereby contributing to the protection of the environment. That is, the quantity of solvents and eluents required in comparison with stepwise processes is considerably reduced. Sequential reactions should, therefore, be more-frequently included in future synthetic planning. In some cases, biogenesis could serve as a prototype, but fundamentally new reaction types must also be developed.

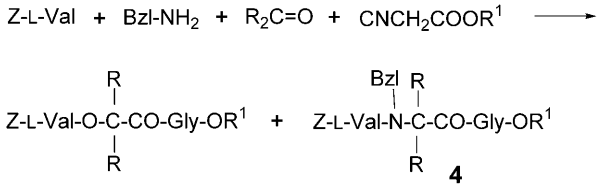
Scheme 4. *Intramolecular Double* Michael *Reaction*



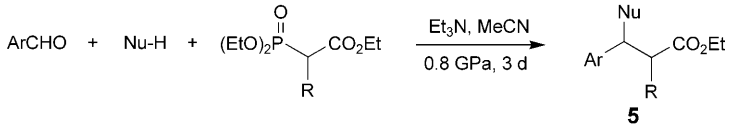
LHMDS = Lithium hexamethyldisilazide

MCRs under high pressure have hardly been studied[1]) [12]. For example, *Yamada et al.* [11e,f] reported the surprising result that a yield of 63 % of the sterically crowded tripeptide **4** was achieved in a modified *Ugi* reaction at high pressure (0.9 GPa; *Scheme 5*). The β-amino ester derivatives **5** were obtained by *Reiser* and co-workers from aldehydes, phosphonates, and N-nucleophiles at 0.8 GPa (*Scheme* 6) [12].

Scheme 5. *Four-Component* Ugi *Reaction at High Pressure*



Scheme 6. Horner–Wadsworth–Emmons–Michael *Domino Reaction at High Pressure*



Nu = N-containing nucleophile

However, high-pressure effects in *Strecker* syntheses have not been investigated, although α-amino nitriles have been prepared for 150 years, since their discovery by *Strecker*. Therefore, we now wish to report, in full detail, on high-pressure-mediated multicomponent *Strecker* reaction of ketones with amines and trimethylsilyl cyanide (Me_3SiCN)[2]).

2. Results and Discussion. – Generally, the *Strecker* reaction without catalyst involves aldehydes as carbonyl compounds [14–16][3]). The analogous reactions with ketones have been rarely studied due to slow or even very slow reaction rates (probably due to steric hindrance). Thus, it was anticipated that ketones in comparison to

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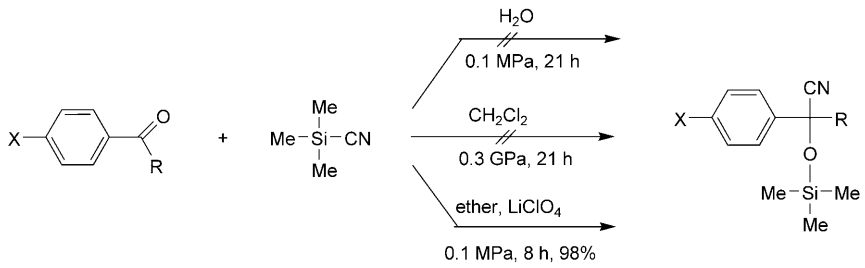
[1]) For examples of high-pressured-promoted MCRs, see [11a–11d] (*Mannich* reaction), [11e,f] (*Ugi* reaction), and [11g,h] (*Passerini* reaction).

[2]) For preliminary communication, see [13].

[3]) For recent examples, see [16b–e].

aldehydes would react under high pressure. In the case of *Michael* and related reactions, the strength of the base was considered, because a carbanion could be obtained from a ketone by deprotonation with the amine. Although this formation of the carbanion was very slow under thermal conditions, it was greatly accelerated at high pressure [17]. By the attack of the carbanion on the carbonyl C-atom of another ketone, the aldol reaction itself can be accelerated by high pressure [18]. Therefore, aromatic amines of very weak basicity were examined to minimize formation of aldol by-products. Me_3SiCN was used as the CN group donor. It readily reacts with ketones in the presence of a *Lewis* acid to form the corresponding organosilicon adducts. However, no reaction between a ketone and Me_3SiCN in the absence of a catalyst, neither at atmospheric nor at high pressure, has been reported [19]. For example, in the absence of catalyst, the cyanosilylation of aromatic ketones by Me_3SiCN did not proceed at 0.1 MPa or 0.3 GPa, *i.e.*, at 1 atm or 300 atm, respectively. However, when an Et_2O solution of $LiClO_4$ was used, the reaction product was obtained at atmospheric pressure in 98% yield (*Scheme 7*).

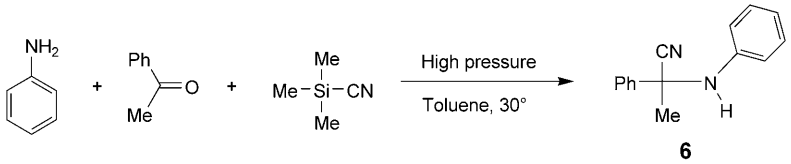
Scheme 7. *Cyanosilylation of Aromatic Ketones with Me_3SiCN*



In the present MCRs, toluene was used as an apolar, aprotic, stable solvent so as not to influence the reaction under high pressure.

First, the effect of pressure change on multicomponent *Strecker* reactions was investigated with acetophenone, aniline, and Me_3SiCN in toluene (*Scheme 8*). The product **6** was obtained under pressures ranging from atmospheric pressure to 0.6 GPa. The MCR did not take place at atmospheric pressure, whereas increased pressure resulted in the accelerated formation of product. A very dramatic effect of increasing pressure from 0.4 to 0.6 GPa was observed, as can be seen from *Fig. 2*. Similar results have been reported by *Jenner* [20], and *Dauben et al.* [21].

Scheme 8. Strecker *Reaction with Acetophenone, Aniline, and Me_3SiCN*



6

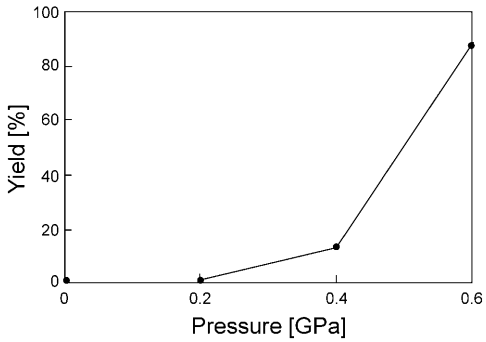
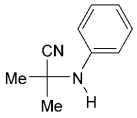
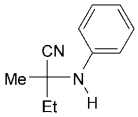
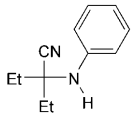
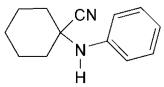
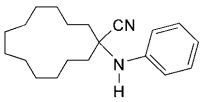


Fig. 2. *Effect of pressure on multicomponent* Strecker *reaction*. Conditions as in *Table 3*.

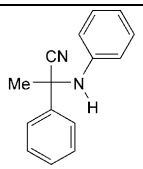
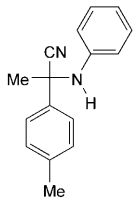
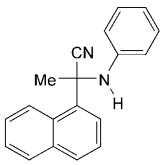
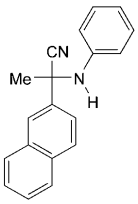
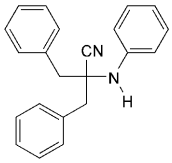
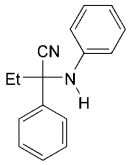
Next, a *Strecker* MCR with several ketones was examined at 0.6 GPa and 30°. The results are summarized in *Tables 3* and *4*. The reactions under high pressure were dependent on the substituent of the ketone. On the whole, when the chain length of ketones increased (*Table 3*, *Entries 1–3*), the yield of compounds **7** was slightly reduced because of the increase in volume. Changes from aliphatic to aromatic

Table 3. *Synthesis of α-Amino Nitriles from Aliphatic Ketones, Aniline, and Me_3SiCN at 0.6 GPa and 30° for 24 h*

Entry	R^1	R^2	Product	No.	Yield[a]) [%]
1	Me	Me		**7a**	99[b])
2	Me	Et		**7b**	98
3	Et	Et		**7c**	95
4		$-(CH_2)_5-$		**7d**	97
5		$-(CH_2)_{12}-$		**7e**	94[c])

[a]) Yields of isolated material based on ketones. [b]) Yield of 22% at atmospheric pressure and r.t. [c]) For 48 h.

Table 4. *Synthesis of α-Amino Nitriles from Aromatic Ketones, Aniline, and Me_3SiCN at 0.6 GPa and 30° for 24 h*

Entry	R^1	R^2	Product	No.	Yield[a]) [%]
1	Me	Ph		**7f**	88
2	Me	4-Me-C_6H_4		**7g**	82
3	Me	1-Naphthyl		**7h**	68
4	Me	2-Naphthyl		**7i**	96
5	Me	9-Anthracenyl	–		0
6	Ph	Ph	–		0
7	Bn	Bn		**7j**	60[b])
8	Et	Ph		**7k**	81

[a]) Yields of isolated material. [b]) At 25°.

substituents (*Table 4*) generally resulted in reduced yields. These results are probably attributed to the increasing steric hindrance around the carbonyl C-atom, and stabilization through delocalization.

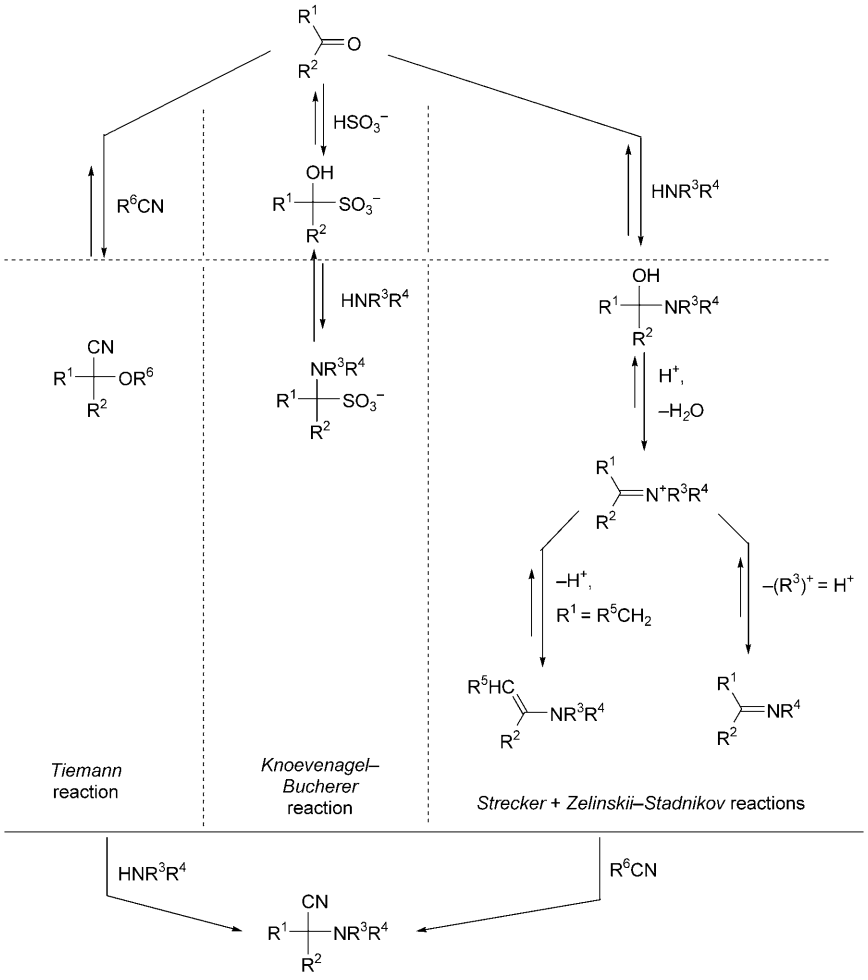
Interestingly for acetonaphthones (*Table 4*, *Entries 3* and *4*), good yields were obtained in contrast to methyl anthracen-9-yl ketone and benzophenone (*Entries 5* and *6*). The reaction leading to **7h** was faster than that affording **7i**, and in the latter, a more-stable intermediate was formed. The lower yield of **7h**, in turn, is due to steric hindrance (*peri*-H effect). These results are in good agreement with those for other ketones. It is apparent that this reaction was retarded by steric hindrance as well as by stabilization through the delocalization of the aromatic substituent of the ketone. At first, it was expected that the addition of aniline to methyl 1-naphthyl ketone could produce a more-compact *Schiff* base as an intermediate than that from other ketones because of the volume reduction under high pressure. In the classical *Strecker* reaction, cyanohydrins [22][23] or imines [24][25] (*via* iminium ions) were formed as intermediates (*Scheme 9*) [26]. However, the low yield of **7h** (*Table 4*) suggests that a *Schiff* base was not formed in the present case. Investigations by *Merino* and co-workers [27] on α-amino nitrile synthesis, by addition of Me_3SiCN to charge-developed nitrone systems, showed that addition of CN^- took place without *Lewis* acids in good yields (*Scheme 10*).

It is interesting that the yield of **7i** (*Table 4*) was better than that of **7f** (*Table 4*). This is perhaps evidence that an iminium ion, which is more stable because of the resonance effect, is formed as an intermediate. Hence, it is likely that the aniline N-atom attacks the C=O group of the ketone to produce an amino alcohol, which, *via* an iminium ion (not an imine), affords the α-amino nitrile by subsequent addition of CN^- (*Scheme 11*).

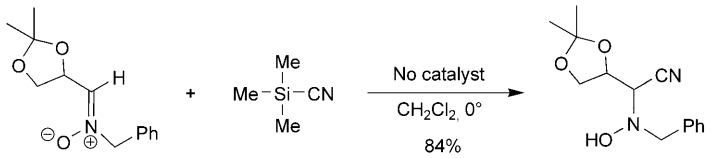
Next, *Strecker* reaction with *N*-methylaniline was examined under high pressure, the base strength of *N*-methylaniline being similar to that of aniline. When acetone and acetophenone were used as ketones, the reactions, unfortunately, did not take place. We think that the inactivity of *N*-methylaniline is due to the steric hindrance of the *N*-methyl group. Therefore, *Strecker* reactions of sterically hindered amines with aldehydes and Me_3SiCN will be the subject of future communications.

In the early days of organic synthesis, only simple molecules could be prepared by rational design. However, over the years, the need for more-complex molecules has arisen in many areas of sciences and technologies. Complex molecules could be synthesized elegantly *via* sequential double reactions like double *Mannich* (for recent examples, see [28]), double *Michael* (for a review, see [29a]; for recent examples, see [29b–d]), and double *Diels–Alder* reactions (for recent examples, see [30a–c]; for examples of double (or consecutive) 1,3-dipolar cycloadditions from our studies, see [30d–g]). However, double *Strecker* reactions have been studied less often. For instance, *Takahashi et al.* [31] reported that double *Strecker* reaction of glutaraldehyde with hydrazine or ethane-1,2-diamine gave heterocyclic 1-amino- or 1-(2-aminoethyl)-2,6-dicyanopiperidine. *Gibson* and co-workers [32] prepared acyclic bis(α-amino nitriles) from aldehyde, sodium bisulfite, amine, and NaCN in high yields by double *Strecker* reaction. These reactions involved aldehydes as the carbonyl compound (for recent examples of double *Strecker* reactions, see [33]). To our knowledge, no double *Strecker* reaction based on *ketones* has been investigated.

Scheme 9. *Comparative Mechanism of* Strecker *Synthesis and Related Reactions*

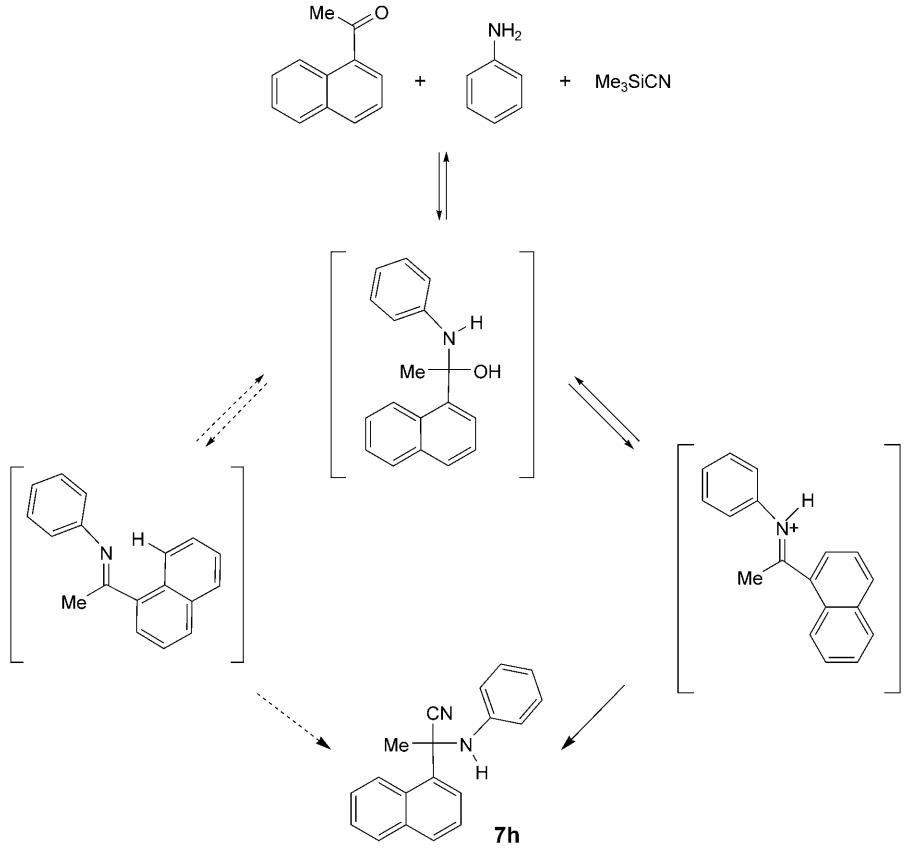


Scheme 10. *Addition of Me_3SiCN to a Charge-Developed System*



First, a double *Strecker* reaction with 1,4-diacetylbenzene, aniline, and Me_3SiCN was attempted under various conditions. The results are summarized in *Table 5*. 1,4-Diacetylbenzene was almost inert at room temperature and atmospheric pressure, even in dipolar solvents. However, at 30° and 0.6 GPa, solvent polarity was found to be

Scheme 11. *Plausible Mechanism of Three-Component* Strecker *Reaction*

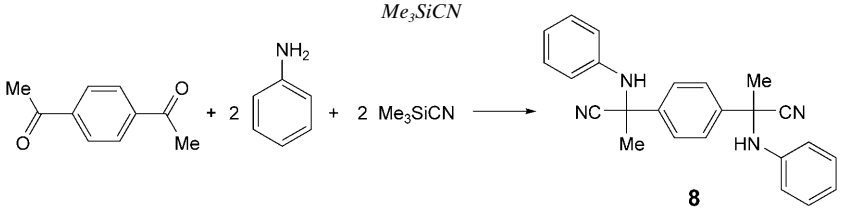


crucial. Investigations of the contributions of solvent polarity were performed by employing the empirical solvent-polarity parameter E_T of *Reichardt*, which is based on solvatochromism of a pyridinium-*N*-phenoxide betain [34–36]. The E_T^N values for toluene, CH_2Cl_2, and MeCN are 0.099, 0.309, and 0.460, respectively. At high pressure, increasing solvent polarity led to an increase in the yield of **8**, with an excellent correlation between E_T^N and yield (*Fig. 3*).

A similar reaction, but with an aliphatic 1,2-diketone, aniline, and Me_3SiCN succeeded at 30° and 0.6 GPa in toluene. However, only 25% of product **9** was obtained (*Scheme 12*).

1,4-Diaminobenzene also underwent another type of double *Strecker* reaction, with different ketones and Me_3SiCN in MeCN at 30° and 0.6 GPa (*Table 6*). When the bulk of substituents around the C=O group increased, the yield was reduced because of increased steric hindrance. The yield of product **10b** was lower than that of **10a**, although the single multicomponent *Strecker* reaction of cyclohexanone proceeded in excellent yield. In organic solvents, **10b** is very unstable, and it is considered that the low yield of this product is due to its instability.

Table 5. *High-Pressure and Solvent Effects on Double* Strecker *Reaction with 1,4-Diacetylbenzene, Aniline, and Me_3SiCN*



Entry	Pressure [GPa]	Solvent	Temp. [°]	Time [h]	Yield[a]) [%]
1	a.p.[b])	THF	r.t.	72	0
2	a.p.	MeCN	r.t.	24	5
3	0.6	Toluene	30	24	0
4	0.6	Toluene	30	48	0
5	0.6	CH_2Cl_2	30	24	48
6	0.6	MeCN	30	24	93

[a]) Yields of isolated material based on diketone. [b]) Ambient pressure.

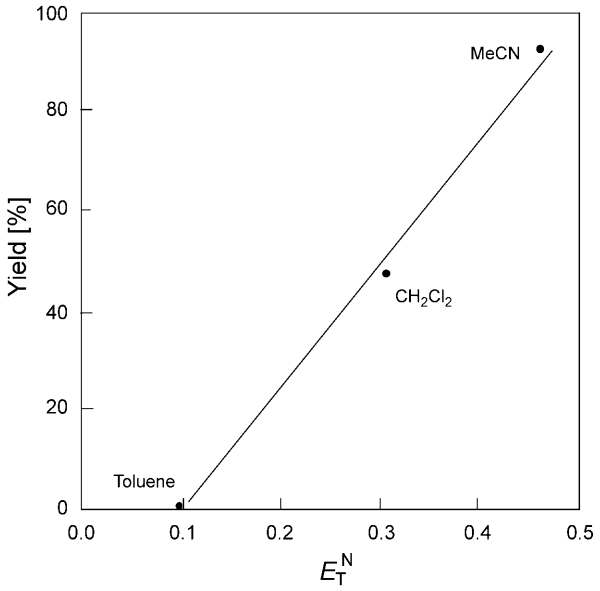


Fig. 3. *Correlation between solvent polarity* (in terms of E_T^N) *and product yield in the high-pressure reaction of 1,4-diacetylbenzene with aniline and Me_3SiCN*

In contrast, methyl 1-naphthyl ketone was inert under these conditions. Similar reactions of ketones with other benzenediamines were also feasible (*Table 7*). For instance, acetone underwent a four-component double *Strecker* reaction in excellent yield, also providing the single *Strecker* product **11e**, which, however, was not stable enough for elemental analysis.

Scheme 12. *Double* Strecker *Reaction with Butane-2,3-dione*

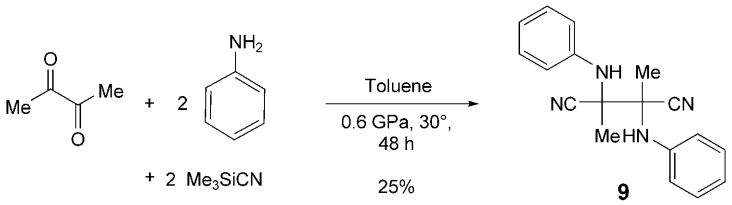
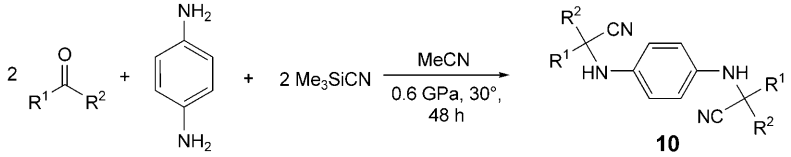
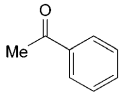
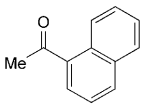


Table 6. *Synthesis of Bis(α-Amino Nitriles) with Benzene-1,4-diamine, Ketones, and Me_3SiCN at 0.6 GPa and 30° for 48 h*



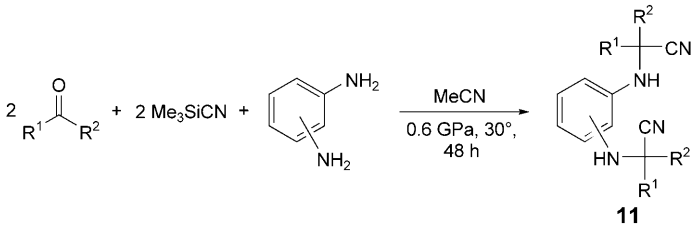
Entry	Ketone	Product	Yield[a]) [%]
1		**10a**	77
2		**10b**	53
3		**10c**	27
4		–	0

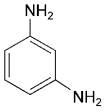
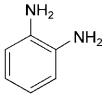
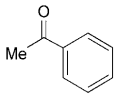
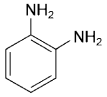
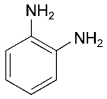
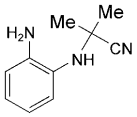
[a]) Yields of isolated material based upon benzene-1,4-diamine.

Unfortunately, triple *Strecker* reactions were unsuccessful in our hands (*Scheme 13*). Further work on application of the present approach to synthesize a variety of heterocyclic compounds in one pot is now in progress.

3. Conclusions. – *Strecker* multicomponent reactions (MCRs) under high pressure between ketones, aromatic amines, and Me_3SiCN in the absence of catalyst were investigated. First of all, the effect of pressure change on *Strecker* MCRs was disclosed with acetophenone, aniline and Me_3SiCN in toluene. Increased pressure led to accelerated formation of product, especially at 0.4 GPa to 0.6 GPa. Next, *Strecker* MCRs with different ketones were examined at 0.6 GPa and 30°. In general, the yield

Table 7. *Synthesis of Bis(α-Amino Nitriles) from Benzenediamines, Ketones, and Me_3SiCN at 0.6 GPa and 30° for 48 h*



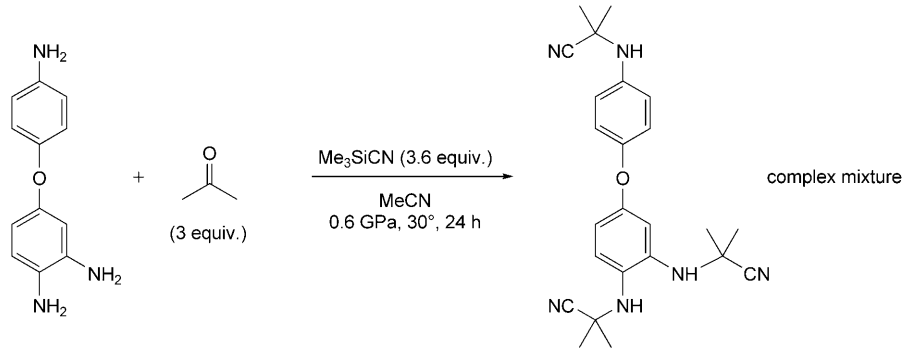
Entry	Ketone	1,3-and 1,2-Diaminobenzene	Product	Yield[a]) [%]
1			**11a**	90
2			**11b**	40
3			**11c**	7
4[b])	 (3 equiv.)		**11d**	91
			**11e**	9

[a]) Yields of isolated material based on diaminobenzene. [b]) 24 h.

was slightly reduced, when the chain length of the ketones increased. Intriguingly, the yield of the product in the case of methyl 2-naphthyl ketone was better than that of methyl phenyl ketone (acetophenone). Thus, presumably, the intermediary iminiun ion, which is more stable because of resonance effects, is formed. A plausible reaction mechanism involves attack of the aniline N-atom at the carbonyl C-atom of the ketone to produce an amino alcohol, which gives an iminium ion (not a *Schiff* base), to which finally CN^- adds to afford the α-amino nitrile.

Double *Strecker* reactions were also shown to be useful under high pressure. The solvent effect of this reaction with 1,4-diacetylbenzene, aniline, and Me_3SiCN was examined. Toluene, THF, CH_2Cl_2, and MeCN were used as solvents. An excellent

Scheme 13. *Attempted Triple* Strecker *Reaction under High Pressure*



linear correlation between solvent polarity (E_T^N) and yield was found, which indicates that the high-pressure double *Strecker* reaction is sensitive to solvent polarity.

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Experimental Part

General. High-pressure reactions: *KP10* or *KP15* instruments (*Hikari High Press, Inc.*, Hiroshima). M.p.: *Yanaco MP-J3* micro-melting-point apparatus; uncorrected. IR Spectra: *Shimadzu FTIR-8600 PC* or *JASCO FT-IR 5300* spectrophotometers; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *JEOL JNM-Ex 270* (270 and 67.8 MHz, resp.) or *JEOL JNM-A 500* (500 and 125.65 MHz, resp.), or *JEOL LA400* (400 and 100 MHz, resp.); in $CDCl_3$ with Me_4Si as internal standard; δ in ppm, J in Hz. Mass spectroscopic data are given in m/z.

Synthesis of 2-Methyl-2-(phenylamino)propanenitrile (**7a**) *at High Pressure.* A soln. of acetone (349 mg, 6.0 mmol), aniline (466 mg, 5.0 mmol), and Me_3SiCN (595 mg, 6.0 mmol) in toluene (6 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was opened. A mixture of a yellow solid and a small amount of soln. was obtained. The solvent was removed by evaporation under reduced pressure. Cyclohexane (6 ml) was added, the solid was filtered off, and dried in vacuum to afford 793 mg of **7a** (99%, based on aniline). Recrystallization from EtOH/H_2O 85 : 15 gave colorless crystals. M.p. 94 – 95°. IR (KBr): 3373, 3030, 2235 (CN). ^1H-NMR (270 MHz): 1.71 (*s*, 6 H); 3.68 (br. *s*, 1 H); 6.91 – 7.29 (*m*, 5 H). ^{13}C-NMR (125.65 MHz): 28.2; 49.1; 117.6; 120.9; 121.8; 129.2; 143.3. MS: 160, 145, 133. Anal. calc. for $C_{10}H_{12}N_2$: C 74.97, H 7.55, N 17.48; found: C 75.13, H 7.59, N 17.58.

Synthesis of **7a** *at Atmospheric* Pressure. A soln. of acetone (349 mg, 6.0 mmol), aniline (466 mg, 5.0 mmol), and Me_3SiCN (595 mg, 6.0 mmol) in toluene (6 ml) was placed in one-neck flask, which was perfectly sealed. The mixture was stirred at r.t. for 24 h. The solvent was removed by evaporation under reduced pressure. Cyclohexane (6 ml) was added, the solid was filtered off, and dried to afford **7a** (173 mg, 22%).

2-Methyl-2-(phenylamino)butanenitrile (**7b**). A soln. of butan-2-one (433 mg, 6.0 mmol), aniline (466 mg, 5.0 mmol), and Me_3SiCN (595 mg, 6.0 mmol) in toluene (6 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was cooled to 0°. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 15 – 20°. Cyclohexane (6 ml) was added, the solid was filtered off, dried in vacuum, and chromatographed (SiO_2; hexane/AcOEt 80 : 20) to afford **7b** (851 mg, 98%, based on aniline). Recrystallization

from EtOH/H_2O 80:20 gave white crystals. M.p. 45–46°. IR (KBr): 3364, 2982, 2237 (CN). ^{1}H-NMR (270 MHz, $CDCl_3$): 1.14 (*t*, *J* = 7.6, 3 H); 1.63 (*s*, 3 H); 1.84–2.06 (*m*, 2 H); 3.61 (br. *s*, 1 H); 6.87–7.29 (*m*, 5 H). ^{13}C-NMR (125.65 MHz): 8.54; 25.2; 33.6; 53.5; 117.3; 120.5; 121.3; 129.1; 143.6. Anal. calc. for $C_{11}H_{14}N_2$: C 75.82, H 8.10, N 16.08; found: C 75.92, H 8.06, N 16.34.

2-Ethyl-2-(phenylamino)butanenitrile (**7c**). A soln. of pentan-3-one (258 mg, 3.0 mmol), aniline (279 mg, 3.0 mmol), and Me_3SiCN (357 mg, 3.6 mmol) in toluene (3.5 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was cooled to 0°. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 15–20°. Cyclohexane (3 ml) was added, the solid was filtered off, dried in vacuum, and chromatographed (SiO_2; hexane/AcOEt 80:20) to afford **7c** (536 mg, 95%, based on ketone). Recrystallization from EtOH/H_2O 80:20 gave white crystals. M.p. 51°. IR (KBr): 3358, 2968, 2241 (CN). ^{1}H-NMR (270 MHz): 1.07 (*t*, *J* = 7.6, 6 H); 1.84–2.07 (*m*, 4 H); 3.55 (br. *s*, 1 H); 6.85–7.26 (*m*, 5 H). ^{13}C-NMR (125.65 MHz): 8.04; 29.6; 57.6; 116.9; 120.2; 120.9; 129.1; 143.8. Anal. calc. for $C_{11}H_{14}N_2$: C 76.55, H 8.57, N 14.88; found: C 76.66, H 8.49, N 14.84.

1-(Phenylamino)cyclohexane-1-carbonitrile (**7d**). A soln. of cyclohexanone (982 mg, 10.0 mmol), aniline (931 mg, 10.0 mmol), and Me_3SiCN (1.191 g, 12.0 mmol) in toluene (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 15–20°. Cyclohexane (8 ml) was added, the solid was filtered off, dried in vacuum, and chromatographed (SiO_2; hexane/AcOEt 80:20) to afford **7d** (1.94 g, 97%, based on ketone). Recrystallization from EtOH/H_2O 85:15 gave white crystals. M.p. 75–76°. IR (KBr): 3354, 2934, 2226 (CN). ^{1}H-NMR (270 MHz): 1.55–1.80 (*m*, 8 H); 2.33 (*m*, 2 H); 3.61 (br. *s*, 1 H); 6.90–7.24 (*m*, 5 H). ^{13}C-NMR (125.65 MHz): 22.2; 24.9; 36.7; 54.4; 117.7; 120.7; 121.1; 129.2; 143.5. Anal. calc. for $C_{13}H_{16}N_2$: C 77.96, H 8.05, N 13.99; found: C 78.10, H 8.11, N 14.17.

1-(Phenylamino)cyclotridecane-1-carbonitrile (**7e**). A soln. of cyclotridecanone (506 mg, 97%, 2.5 mmol), aniline (233 mg, 2.5 mmol), and Me_3SiCN (298 mg, 3.0 mmol) in toluene (2.5 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 48 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 15–20°. Cyclohexane (3 ml) was added, the solid was filtered off, and dried in vacuum to afford **7e** (0.70 g, 94%, based on ketone). Recrystallization from toluene gave white crystals. M.p. 135–136°. IR (KBr): 3381, 2928, 2241 (CN). ^{1}H-NMR (270 MHz): 1.36 (*s*, 20 H); 1.97 (*m*, 4 H); 3.63 (br. *s*, 1 H); 6.87–7.24 (*m*, 5 H). ^{13}C-NMR (125.65 MHz): 20.5; 25.15; 25.22; 26.3; 26.9; 35.3; 55.7; 116.4; 119.9; 121.2; 129.1; 143.5. Anal. calc. for $C_{13}H_{16}N_2$: C 80.48, H 10.13, N 9.39; found: C 80.29, H 9.95, N 9.28.

2-Phenyl-2-(phenylamino)propanenitrile (**7f**). A soln. of acetophenone (481 mg, 4.0 mmol), aniline (373 mg, 4.0 mmol), and Me_3SiCN (476 mg, 4.8 mmol) in toluene (4 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (5 ml) was added, the solid was filtered off, and dried in vacuum to afford **7f** (780 mg, 88%, based on ketone). Recrystallization from EtOH/H_2O 80:20 gave white crystals. M.p. 139–140°. IR (KBr): 3387, 2990, 2228 (CN). ^{1}H-NMR (270 MHz): 1.95 (*s*, 3 H); 4.27 (br. *s*, 1 H); 6.52–7.64 (*m*, 10 H). ^{13}C-NMR (125.65 MHz): 33.4; 57.1; 115.8; 120.0; 120.7; 124.9; 128.6; 129.0; 129.2; 139.9; 143.5. Anal. calc. for $C_{15}H_{14}N_2$: C 81.05, H 6.35, N 12.60; found: C 81.06, H 6.39, N 12.59.

2-(4-Methylphenyl)-2-(phenylamino)propanenitrile (**7g**). A soln. of methyl 4-methylphenyl ketone (1.342 g, 10.0 mmol), aniline (931 mg, 10.0 mmol), and Me_3SiCN (1.489 g, 15.0 mmol) in toluene (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (8 ml) was added, the solid was filtered off, and dried in vacuum to afford **7g** (1.94 g, 82%, based on ketone). Recrystallization from EtOH/H_2O 80:20) gave white crystals. M.p. 128–129°. IR (KBr): 3387, 2986, 2228 (CN). ^{1}H-NMR (270 MHz): 1.93 (*s*, 3 H); 2.36 (*s*, 3 H); 4.25 (br. *s*, 1 H); 6.53–7.51 (*m*, 9 H). ^{13}C-NMR (125.65 MHz): 21.0; 33.3; 56.8; 115.5; 119.7; 120.6; 124.6; 128.7; 129.6; 136.7; 138.2; 143.3. Anal. calc. for $C_{15}H_{14}N_2$: C 81.32, H 6.82, N 11.85; found: C 81.42, H 6.90, N 11.75.

2-(Naphthalen-1-yl)-2-(phenylamino)propanenitrile (**7h**). A soln. of methyl naphthalen-1-yl ketone (851 mg, 5.0 mmol), aniline (466 mg, 5.0 mmol), and Me_3SiCN (595 mg, 6.0 mmol) in toluene (6 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was

removed by evaporation under reduced pressure at 20–25°. Cyclohexane (6 ml) was added, the solid was filtered off, and dried in vacuum to afford **7h** (931 mg, 68%, based on ketone). Recrystallization from EtOH gave white crystals. M.p. 124–126°. IR (KBr): 3373, 3003, 2230 (CN). ^{1}H-NMR (270 MHz): 2.25 (*s*, 3 H); 4.35(br. *s*, 1 H); 6.64–8.83 (*m*, 12 H). ^{13}C-NMR (125.65 MHz): 30.3; 57.8; 116.3; 120.3; 121.2; 124.3; 125.09; 125.14; 125.9; 126.5; 129.0; 129.3; 129.4; 130.2; 133.3; 134.8; 143.6. Anal. calc. for $C_{15}H_{14}N_2$: C 83.79, H 5.92, N 10.29; found: C 83.71, H 5.98, N 10.24.

2-(Naphthalen-2-yl)-2-(phenylamino)propanenitrile (**7i**). A soln. of methyl naphthalen-2-yl ketone (511 mg, 3.0 mmol), aniline (279 mg, 3.0 mmol), and Me_3SiCN (357 mg, 3.6 mmol) in toluene (3 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (3 ml) was added, the solid was filtered off, and dried in vacuum to afford **7i** (801 mg, 98%, based on ketone). Recrystallization from EtOH gave white crystals. M.p. 176–177. IR (KBr): 3381, 2988, 2228 (CN). ^{1}H-NMR (270 MHz): 2.02 (*s*, 3 H); 4.34 (br. *s*, 1 H); 6.57–8.14 (*m*, 12 H). ^{13}C-NMR (500 MHz): 33.3; 57.4; 115.9; 120.1; 120.7; 122.1; 124.4; 126.7; 127.7; 128.3; 129.1; 129.4; 133.2; 133.3; 137.4; 143.5. MS: 272, 245, 230, 118, 77. Anal. calc. for $C_{15}H_{14}N_2$: C 83.79, H 5.92, N 10.29; found: C 83.51, H 6.08, N 10.17.

3-Phenyl-2-(phenylamino)-2-(phenylmethyl)propanenitrile (**7j**). A soln. of 1,3-diphenylpropan-2-one (1.893 g, 9.0 mmol), aniline (838 mg, 9.0 mmol), and Me_3SiCN (1.071 g, 10.8 mmol) in toluene (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 25° for 24 h. After returning to atmospheric pressure, the capsule was cooled to 0°. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 15–20°. Cyclohexane (8 ml) was added, the solid was filtered off, and dried in vacuum to afford **7j** (1.68 g, 60%, based on ketone). Recrystallization from EtOH gave white crystals. M.p. 130–131°. IR (KBr): 3337, 3032, 2245 (CN). ^{1}H-NMR (270 MHz): 3.16 (*dd*, $J = 13.8$, 30.5, 4 H); 3.76 (br. *s*, 1 H); 6.90–7.38 (*m*, 15 H). ^{13}C-NMR (125.65 MHz): 43.5; 47.5; 117.8; 120.7; 127.0; 127.4; 127.8; 128.3; 128.9; 130.2; 130.5. Anal. calc. for $C_{15}H_{14}N_2$: C 84.58, H 6.45, N 8.97; found: C 84.69, H 6.66, N 8.83.

2-Phenyl-2-(phenylamino)butanenitrile (**7k**). A soln. of ethyl phenyl ketone (671 mg, 5.0 mmol), aniline (466 mg, 5.0 mmol), and Me_3SiCN (695 mg, 7.0 mmol) in toluene (5 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (5 ml) was added, the solid was filtered off, and dried in vacuum to afford **7k** (780 mg, 88%, based on ketone). Recrystallization from EtOH/H_2O 80:20 gave white crystals. M.p. 142–143°. IR (KBr): 3381, 2970, 2237 (CN). ^{1}H-NMR (270 MHz): 1.06 (*t*, $J = 7.6$, 3 H); 2.15 (*m*, 2 H); 4.27 (br. *s*, 1 H); 6.52–7.60 (*m*, 10 H). ^{13}C-NMR (125.65 MHz): 8.8; 38.4; 62.1; 115.7; 119.9; 125.7; 128.6; 128.99; 129.03; 138.3; 143.6. Anal. calc. for $C_{16}H_{16}N_2$: C 81.32, H 6.82, N 11.85; found: C 81.39, H 6.81, N 11.93.

2,2′-(1,4-Phenylene)bis[2-(phenylamino)propanenitrile] (**8**). A soln. of 1,4-diacetylbenzene (243 mg, 1.5 mmol), aniline (279 mg, 3.0 mmol), and Me_3SiCN (357 mg, 3.6 mmol) in MeCN (3 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 24 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (3 ml) was added, and the solid was filtered off, washed with anh. Et_2O, and dried in vacuum to afford **8** (93%, based on diketone) as a white solid. M.p. 208–210. IR (KBr): 3381, 3055, 2228 (CN). ^{1}H-NMR (270 MHz): 1.95 (*s*, 6 H); 4.29 (br. *s*, 2 H); 6.50 (*d*, $J = 7.8$, 4 H); 6.81 (*t*, $J = 7.6$, 2 H); 7.11 (*t*, $J = 7.3$, 4 H); 7.66 (*s*, 4 H). ^{13}C-NMR (125.65 MHz): 32.2; 56.2; 115.0; 118.2; 120.8; 125.5; 128.4; 140.8; 144.5. Anal. calc. for $C_{24}H_{22}N_4$: C 78.66, H 6.05, N 15.29; found: C 78.45, H 6.04, N 15.32.

2,3-Dimethyl-2,3-bis(phenylamino)butane-1,4-dinitrile (**9**). A soln. of butane-2,3-dione (215 mg, 2.5 mmol), aniline (466 mg, 5.0 mmol), and Me_3SiCN (595 mg, 6.0 mmol) in toluene (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 48 h. After returning to atmospheric pressure, the capsule was opened. A yellow solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (5 ml) was added, the solid was filtered off, washed with toluene, and dried in vacuum to afford **9** (25%, based on diketone) as a white solid. M.p. 125–126°. IR (KBr): 3360, 3053, 2249 (CN). ^{1}H-NMR (270 MHz): 1.72 (*s*, 6 H); 4.24 (br. *s*, 2 H); 7.16–7.40 (*m*, 10 H). ^{13}C-NMR (125.65 MHz): 20.0; 62.5; 119.1; 124.7; 125.3; 129.5; 141.5. Anal. calc. for $C_{24}H_{22}N_4$: C 74.46, H 6.25, N 19.30; found: C 74.22, H 6.38, N 19.01.

2,2′-(1,4-Phenylenediimino)bis(2-ethylbutanenitrile) (**10a**). A soln. of pentan-3-one (517 mg, 6.0 mmol), 1,4-phenylenediamine (315 mg, 2.9 mmol), and Me_3SiCN (714 mg, 7.2 mmol) in MeCN (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 48 h. After returning to atmospheric pressure, the capsule was opened. A solid and a small amount of soln. were obtained. The solvent was removed by

evaporation under reduced pressure at 20–25°. Cyclohexane (8 ml) was added, the solid was filtered off, washed with anh. EtOH, and dried in vacuum to afford **10a** (675 mg, 79%, based on diamine). M.p. 131–132°. IR (KBr): 3389, 2982, 2222 (CN). ^{1}H-NMR (270 MHz): 1.07 (*t*, *J* = 7.6, 12 H); 1.89 (*m*, 8 H); 3.31 (br. *s*, 2 H); 6.89 (*s*, 4 H). ^{13}C-NMR (125.65 MHz): 8.0; 29.5; 58.8; 120.7; 121.4; 138.1. Anal. calc. for $C_{18}H_{26}N_4$: C 72.44, H 8.78, N 18.77; found: C 72.27, H 8.92, N 19.03.

1,1′-(1,4-Phenylenediimino)bis(cyclohexanecarbonitrile) (**10b**). A soln. of cyclohexanone (295 mg, 3.0 mmol), 1,4-phenylenediamine (165 mg, 1.5 mmol), and Me_3SiCN (357 mg, 3.6 mmol) in MeCN (3 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 48 h. After returning to atmospheric pressure, the capsule was opened. A solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 15–20°. Cyclohexane (3 ml) was added, the solid was filtered off, washed with anh. EtOH and cyclohexane, and dried in vacuum to afford **10b** (253 mg, 53%, based on diamine). M.p. 156–158°. IR (KBr): 3371, 2932, 2228 (CN). ^{1}H-NMR (270 MHz): 1.57–2.24 (*m*, 20 H); 3.38 (br. *s*, 2 H); 6.91 (*s*, 4 H). ^{13}C-NMR (125.65 MHz): 22.3; 25.0; 36.6; 55.5; 121.5; 138.2. Anal. calc. for $C_{20}H_{26}N_4$: C 74.50, H 8.13, N 17.38; found: C 74.20, H 8.03, N 17.54.

2,2′-(1,4-Phenylenediimino)bis(2-phenylpropanenitrile) (**10c**). A soln. of acetophenone (721 mg, 6.0 mmol), 1,4-phenylenediamine (315 mg, 2.9 mmol), and Me_3SiCN (714 mg, 7.2 mmol) in MeCN (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 48 h. After returning to atmospheric pressure, the capsule was opened. A solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (8 ml) was added, and the solid was filtered off, washed with anh. EtOH, and dried in vacuum to afford **10c** (286 mg, 27%, based on diamine). M.p. 140–142°. IR (KBr): 3389, 3001, 2232 (CN). ^{1}H-NMR (270 MHz): 1.87 (*s*, 3 H); 6.39–7.58 (*m*, 7 H). ^{13}C-NMR (125.65 MHz): 32.4; 57.0; 115.5; 116.1; 124.6; 128.1; 128.9; 137.2; 141.0. MS: 366, 340, 326, 312, 297, 281, 195, 77.

2,2′-(1,3-Phenylenediimino)bis(2-ethylbutanenitrile) (**11a**). A soln. of pentan-3-one (517 mg, 6.0 mmol), 1,3-phenylenediamine (315 mg, 2.9 mmol), and Me_3SiCN (714 mg, 7.2 mmol) in MeCN (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 48 h. After returning to atmospheric pressure, the capsule was opened. A solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (8 ml) was added, and the solid was filtered off, washed with anh. EtOH, and dried in vacuum to afford **11a** (806 mg, 90%, based on diamine). M.p. 107–109°. IR (KBr): 3406, 2978, 2222 (CN). ^{1}H-NMR (270 MHz): 1.07 (*t*, *J* = 7.6, 12 H); 1.98 (*m*, 8 H); 3.55 (br. *s*, 2 H); 6.38 (*dd*, *J* = 2.4, 7.8, 2 H); 6.48 (*t*, *J* = 2.4, 1 H); 7.06 (*t*, *J* = 8.1, 1 H). ^{13}C-NMR (125.65 MHz): 8.0; 29.6; 57.4; 104.1; 108.7; 121.0; 130.0; 144.9. Anal. calc. for $C_{18}H_{26}N_4$: C 72.44, H 8.78, N 18.77; found: C 72.49, H 8.59, N 18.67.

2,2′-(1,2-Phenylenediimino)bis(2-ethylbutanenitrile) (**11b**). A soln. of pentan-3-one (517 mg, 6.0 mmol), 1,2-phenylenediamine (324 mg, 3.0 mmol), and Me_3SiCN (714 mg, 7.2 mmol) in MeCN (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 48 h. After returning to atmospheric pressure, 1N aq. HCl soln. (50 ml) was added to the reaction mixture. The mixture was extracted with AcOEt, the org. layer was dried (Na_2SO_4) and concentrated *in vacuo* at 20–25°, and the residue was chromatographed (SiO_2; hexane/AcOEt 80:20) to afford **11b** as an oil (365 mg, 40%, based on diamine). IR (KBr): 3312, 2976, 2226 (CN). ^{1}H-NMR (270 MHz): 1.06 (*t*, *J* = 7.6, 12 H); 1.88 (*m*, 8 H); 3.90 (br. *s*, 2 H); 6.96–7.30 (*m*, 4 H). ^{13}C-NMR (125.65 MHz, $CDCl_3$): 8.1; 29.4; 58.6; 120.0; 121.4; 122.8; 135.6. Anal. calc. for $C_{18}H_{26}N_4$: C 72.44, H 8.78, N 18.77; found: C 72.16, H 8.67, N 18.72.

2,2′-(1,2-Phenylenediimino)bis(2-phenylpropanenitrile) (**11c**). A soln. of acetophenone (721 mg, 6.0 mmol), 1,2-phenylenediamine (324 mg, 3.0 mmol), and Me_3SiCN (714 mg, 7.2 mmol) in MeCN (8 ml) was placed in a *Teflon* capsule. Pressure was applied at 0.6 GPa and 30° for 48 h. After returning to atmospheric pressure, the capsule was opened. A solid and a small amount of soln. were obtained. The solvent was removed by evaporation under reduced pressure at 20–25°. Cyclohexane (8 ml) was added, the solid was filtered off, washed with anh. EtOH, and dried in vacuum to afford **11c** (72 mg, 7%, based on diamine). M.p. 143–145°. IR (KBr): 3348, 2991, 2224 (CN). ^{1}H-NMR (270 MHz): 1.98 (*s*, 6 H); 4.28 (br. *s*, 2 H); 6.72–7.65 (*m*, 14 H). ^{13}C-NMR (125.65 MHz): 32.1; 57.9; 119.5; 121.2; 122.5; 125.0; 128.9; 129.3; 134.3; 139.5. MS: 366, 339, 324, 312, 297, 284, 195, 77. Anal. calc. for $C_{24}H_{22}N_4$: C 78.66, H 6.05, N 15.29; found: C 78.44, H 6.18, N 15.35.

2,2′-(1,2-Phenylenediimino)bis(2-methylpropanenitrile) (**11d**). This compound was prepared in analogy to **11a** in 91% yield. As a side product, *2-[(2-aminophenyl)amino]-2-methylpropanenitrile* (**11e**) was obtained in 9% yield.

Data of **11d**. Colorless solid. M.p. 80–82°. IR (KBr): 3302, 2226 (CN), 1599, 1509. ^{1}H-NMR (400 MHz): 1.64 (*s*, 12 H); 3.91 (br. *s*, 2 H); 7.02, 7.27 (2*m*, 2 × 2 H). ^{13}C-NMR (100 MHz) 27.95; 49.83; 120.14; 122.46; 123.12; 135.59. Anal. calc. for $C_{14}H_{18}N_4$: C 69.39, H 7.49, N 23.12; found: C 69.15, H 7.68, N 23.05.

Data of **11e**. Colorless oil that decomposed at elevated temperatures. IR (neat): 3320, 2224, 1612, 1504, 1456. ^{1}H-NMR (400 MHz): 1.62 (*s*, 6 H); 3.19 (br., 1 H); 3.70 (br., 2 H); 6.75 (*dd*, *J* = 7.8, 1.5, 1 H); 6.79 (*dt*, *J* = 7.8, 1.5, 1 H); 6.95 (*dt*, *J* = 7.8, 1.2, 1 H); 7.28 (*dd*, *J* = 7.8, 1.2, 1 H). ^{13}C-NMR (100 MHz): 27.76; 50.62; 116.36; 119.36; 122.97; 123.11; 124.85; 130.14; 141.47.

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