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Quantitative Solid-State Reactions of Amines with Carbonyl Compounds and Isothiocyanates

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Abstract—A series of solid-state reactions is reported of gaseous or solid amines with aldehydes to give imines, with solid anhydrides to give diamides (therefrom imides) or amidic carboxylic salts or imides, with solid imides to give diamides, with solid lactones or carbonates to give functionalized carbamic esters, with polycarbonates to give degradative aminolysis, and with solid isothiocyanates to give thioureas. Diamides give imides by solid-state thermolysis or acid catalysis. Various double, two-step, 3-cascade, and sequential reactions are reported in the solid state without melting. The yields are quantitative in 53 reported reaction examples and no workup (except for washings in four cases) is required in the 100% yield reactions. Three initially solid-state reactions but with liquid product were not quantitative. An upscaling to the kg scale shows promise of the technique for large scale applications. Supermicroscopic analyses with AFM elucidate the solid-state mechanism by virtue of far-reaching anisotropic molecular movements in three-step processes. Gas–solid aminolyses of polycarbonates are also studied with AFM. The implications to sustainable chemistry are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Solid-state reactions proceed quantitatively if the three requirements are met that govern such environmentally benign processes: (1) in the phase rebuilding step molecules must be able to move far distances in the crystal; (2) the phase transformation step deals with unhindered crystallization of the product; and (3) disintegration of the new phase from the old one is essential to create fresh surface for continuation of the reaction to completion.[1] While these three requirements are not met in all thermodynamically possible combinations, many useful reactions (including cascade reactions) with 100% yield and no necessity for workup have been reported. In some cases favorable conditions could be created by proper experimentation, in order to attain full benefit from avoiding wastes and saving resources. We report here on various quantitative gas–solid and solid–solid reactions with primary or secondary amines that proceed with unsurmounted efficiency, much better than in solutions or melts. While no mechanical treatment is required in most gas–solid reactions (unless there is gas formation), solid–solid reactions require cogrinding, or ultrasound treatment or most easily reactive milling.

Results and Discussion

Nucleophilic additions to aldehydes

Numerous quantitative syntheses of imines have been

Table 1. Gas–solid syntheses of *N*-alkyl-azomethines

1	R	R′	Mp (°C)	**2/3** R″	Yield (%)	$\nu_{C=N}$ (cm^{-1})	Mp (°C)	Lit. mp (°C)	Lit.
a	NO_2	H	105–108	CH_3	100	1648	106	107	3
				C_2H_5	100	1645	76	76–77	4
b	OH	H	117–119	CH_3	100	1647	175	178–180	5
				C_2H_5	100	1643	198		6
c	$N(CH_3)_2$	H	73–75	CH_3	100	1639	54	54	3
				C_2H_5	100	1641	64		6a
d	OCH_3	OCH_2Ph	196–197	CH_3	100	1645	66	67.5–68.5	7
				C_2H_5	100	1647	75		
e	9-formyl-anthracene		104–105	CH_3	100	1634	113	113	8
				C_2H_5	100	1637	76	76–77	8

Keywords: solid-state synthesis; quantitative yield; sustainable chemistry; amines; carbonyl compounds; isothiocyanates; multistep reactions.
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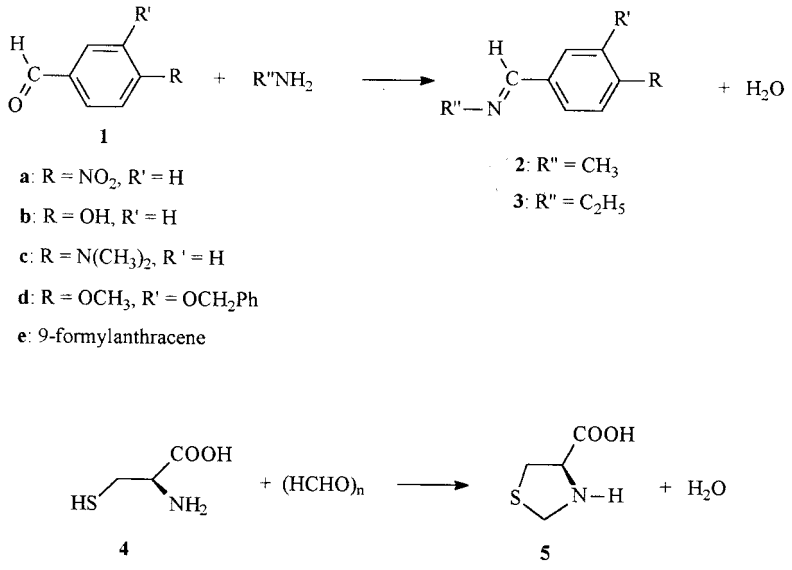


Scheme 1. Quantitative imine syntheses (and trapping) with gaseous or solid amines and solid aldehydes including paraformaldehyde.

performed in the absence of acid catalysis in the solid-state.[2] Such behavior can be extended to gas–solid reactions with aliphatic amines. Thus, solid aldehydes **1** condense with methyl- or ethylamine and the crystalline imines **2** are obtained quantitatively (Table 1). The water of reaction is included in the crystals and can be removed by heating to 80°C in a vacuum (Scheme 1).

Most of the *N*-alkyl-azomethines of Table 1 have been previously prepared in solution reactions (e.g. benzene, toluene, ethanol), although never with quantitative yields. Thus, only the gas–solid technique is able to prevent waste formation, in particular as no workup (except evacuation drying) is required.

These solid-state reactions profit from the crystal packing. The absence of (nano)liquid phases[1] and the anisotropic molecular movements are shown for **1b** and methylamine by stable atomic force microscopic (AFM) images (Fig. 1).

The rather flat initial (010)-surface of **1b** (R_{ms}=1.07 nm) in Fig. 1a is changed to a rougher structure with hills and

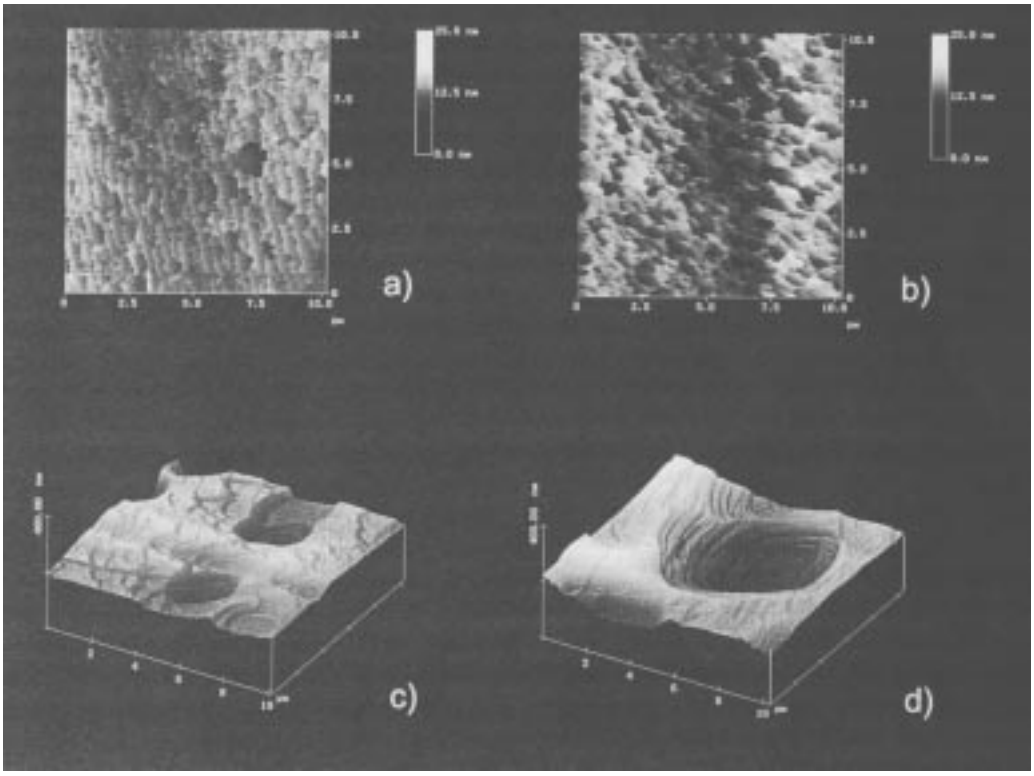


Figure 1. AFM topographies of 4-hydroxybenzaldehyde **1b** on (010): (a) fresh; (b) after 1 min exposure to 0.1 mL ethylamine; (c) after 1 min exposure to 0.2 mL ethylamine; (d) after 1 min exposure to 0.4 mL ethylamine; the scan direction is at right angle to the long crystal edge.

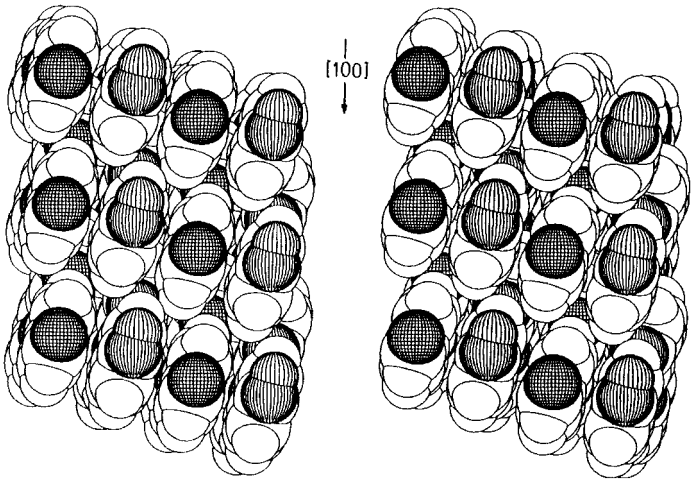
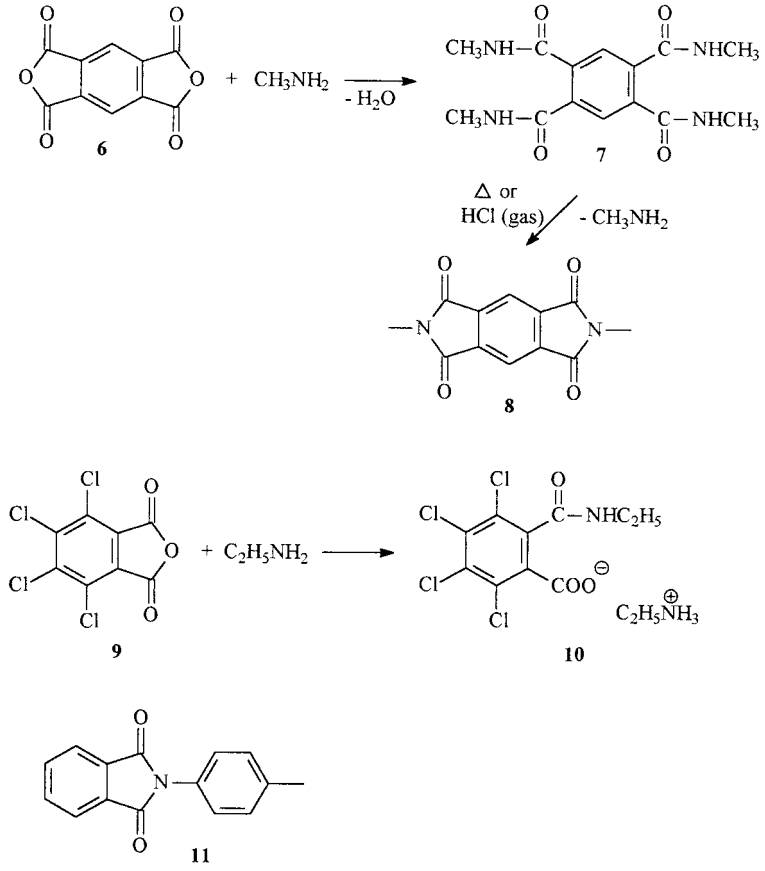


Figure 2. Stereoscopic space filling view of the molecular packing of 4-hydroxybenzaldehyde (**1b**) on (010); OH with meridians; carbonyl O with grid.

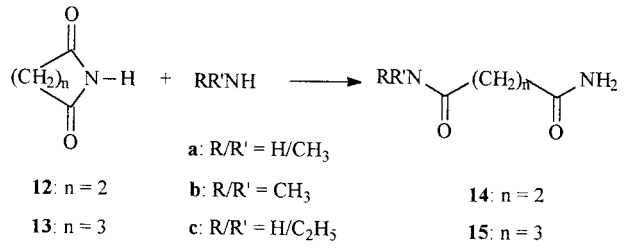
craters all over the plane (R_{ms}=2.95 nm) in Fig. 1b. Doubling the chemical exposure leads to huge changes with formation of craters and steps (Fig. 1c) that become more pronounced upon further reaction in Fig. 1d, shortly before the disintegration of the crystal occurs. The initial phase rebuilding is correlated to the crystal packing (Fig. 2).[9]

It is seen, that the molecules stand vertical on that face and that half of them expose their carbonyl oxygen, the other half their hydroxyl group. Thus, the reaction can start everywhere on (010) at the phase rebuilding stage and the molecules must move above that surface while forming almost uniform hills and craters. By doing so hydrogen bonds of 1.751 Å length have to be broken in the bulk. The max/min distances reach up to 10 nm in Fig. 1b.

The next reaction stage enters totally different dimensions and it is not expected that the crystal structure of **1b** guides the phase transformation features that are growing in width but not in height until disintegration with creation of fresh surface for further reaction.



Scheme 2. Quantitative gas–solid and solid–solid reactions of phthalic anhydrides with amines; solid state imide formation.



Scheme 3. Quantitative gas–solid ring opening of aliphatic imides with gaseous amines.

Aliphatic aldehydes can also be used in solid-state condensation of amines, however, it is not convenient to use gaseous formaldehyde. Interestingly, solid paraformaldehyde may be used instead, most conveniently in a ball mill. Thus, milling of stoichiometric quantities of (L)-cysteine **4** and $(HCHO)_n$ yields a quantitative yield of the (*R*)-thiazolidine **5** within 1 h. The crystal water is removed at 80°C in a vacuum. Both NH_2 and SH react and/or trap in this cyclization. Such use of paraformaldehyde is a considerable step forward in sustainable chemistry and numerous further condensation reactions can be envisioned.[10]

Nucleophilic additions to phthalic anhydrides

While previous quantitative and waste-free reactions of amines have been concentrated on reactions with aldehydes and ketones it is also possible to react solid carboxylic anhydrides. Benzoic anhydrides have been reacted with gaseous ammonia to give mixtures of benzamides and ammonium salts.[11] It was therefore of interest to check, if phthalic anhydrides would be candidates for quantitative ring openings with aliphatic gaseous amines in a waste-free manner (Scheme 2).

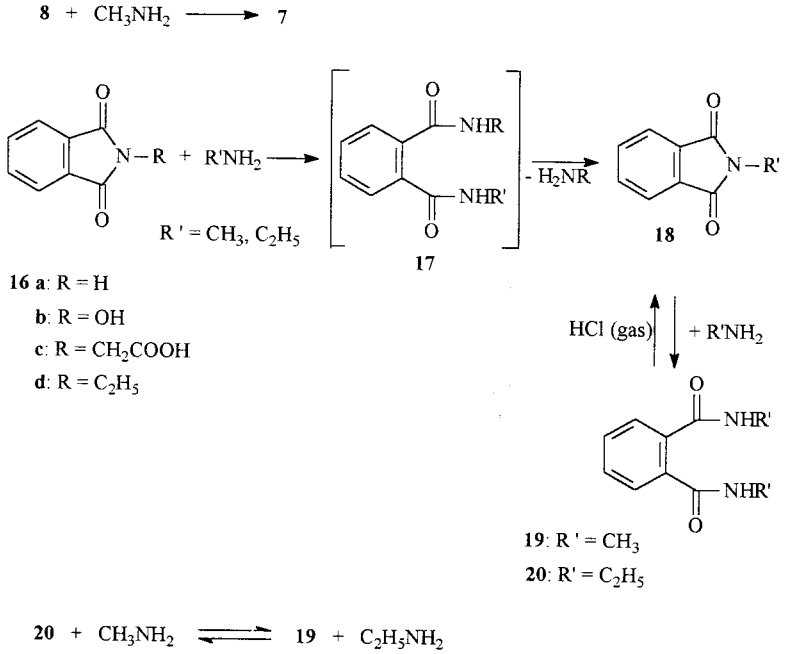
It is of high interest, that these syntheses proceed easily and with quantitative yield. Thus, gas–solid interaction of pyromellitic dianhydride **6** with methylamine provides the tetraamide **7** in quantitative yield. This reaction is highly exothermic initially (a 2 mmol run heated itself up to 95°C for 2 min and distilled water of reaction to the walls of the flask), but melting was avoided. Solid **7** loses two methylamine to give **8**[12] quantitatively in a novel solid-state thermal reaction when heated to 160°C in a vacuum. The same conversion occurs as a gas–solid reaction if **7** is treated with gaseous HCl at RT.

The tetrachlorophthalic anhydride **9** yielded the amidic carboxylic salt **10** quantitatively when reacted with gaseous ethylamine, though less violently. A third type of result was obtained in the solid–solid reaction of phthalic anhydride and 4-toluidine. When these components were ball-milled in a 1:1 ratio, a quantitative yield of the imide **11** ensued directly.

The reaction of **9** to give **10** was upscaled to 500 g runs[13] in a rotary evaporator setup with constant supply of ethylamine from a steel container. Unlike the gram scale runs the material did aggregate at about 70% conversion and full reaction could only be achieved after intermediate grinding. Clearly there is some difficulty with step 3 of the crystal mechanism (creation of fresh surface) that would require some moderate grinding setup or an efficient fluidized bed in technical scale syntheses of **10**. It may be expected that these versatile quantitative reactions of anhydrides will also work with different amines and anilines.

Nucleophilic additions to imides

The solid-state reactions of succinimide **12** and glutarimide **13** with gaseous amines provide the diamides **14**, **15** with two different amide functions in quantitative yield. While **12**



Scheme 4. Quantitative gas–solid reactions of imides and diamides; equilibration of diamides.

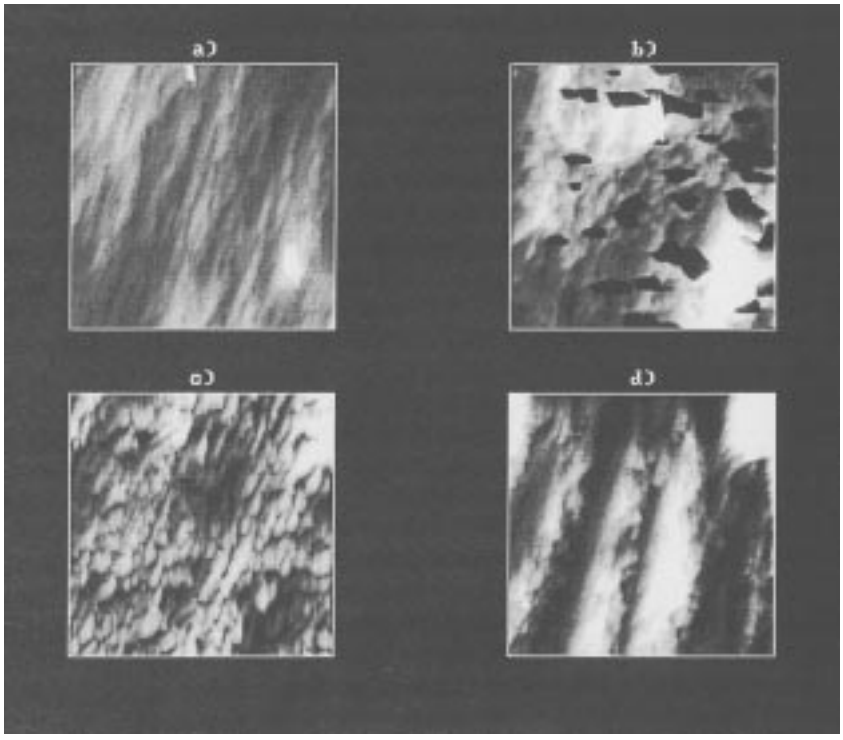


Figure 3. AFM topographies of phthalimide **16a** on (001): (a) fresh; (b) after 1 min exposure to 3 mL $EtNH_2$; (c) after 1 min exposure to 6 mL $EtNH_2$; (d) after 1 min exposure to 9 mL $EtNH_2$ in air; the *z*-scale is 50 nm; the scanning angle is 70–75° to the long crystal edge.

reacts readily at room temperature, **13** requires heating to 80°C in order to avoid intermediate liquefying (Scheme 3). Here, apparently, the phase transformation (step 2) is not fast enough at room temperature and 50°C but can be sufficiently enhanced at 80°C to provide a 100% yield. Some products **14** were reported in liquid phase with yields of 99% (**14a**) and unspecified.[14] The reaction of phthalimides with methyl- or ethylamine is totally different: symmetric diamides or tetramides are formed in solid-state 3-cascade reactions by apparent ring-opening, ring-closure and ring-opening. Thus, the solid diimide **8** and gaseous methylamine give **7** quantitatively (two 3-cascades). This observation suggests that **8** may be an intermediate in the reaction of **6** to give **7** (Scheme 4).

In the case of the imides **16a–c** gaseous methyl- or ethylamine open the 5-membered ring to give the diamides **17** that do not survive. NH_3 or NH_2OH or $H_2NCH_2CO_2H$ are split off presumably via base catalyzed ring closure and the stronger nucleophile which is present in excess attacks for a second time to yield **19** or **20** quantitatively. Similarly, solid **16d** was reacted with ethylamine to give **20**. The imide mechanism was substantiated further by the equilibration of **19** with **20** in the solid state with methylamine at RT. Such imide formation is also obtained by gas–solid reaction of **19** or **20** with HCl. For synthetic purposes it is advisable to choose equal alkyl groups in the amide and amine (as done with **8** or **16d**) in order to avoid separation of gas mixtures or washing away of glycine with water. A similar reaction of **16a** and ethylamine has been realized in solution though with only 50% yield (**19**).[15]

It is amazing that the solid-state 3-cascade reactions[16] run to completion without intermediate melting. The reason is to

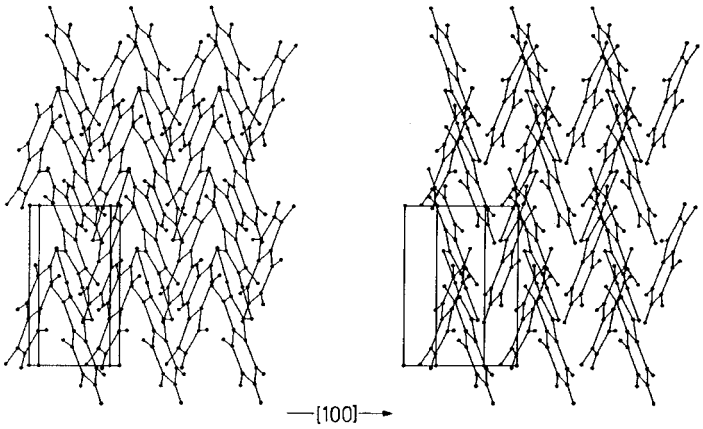
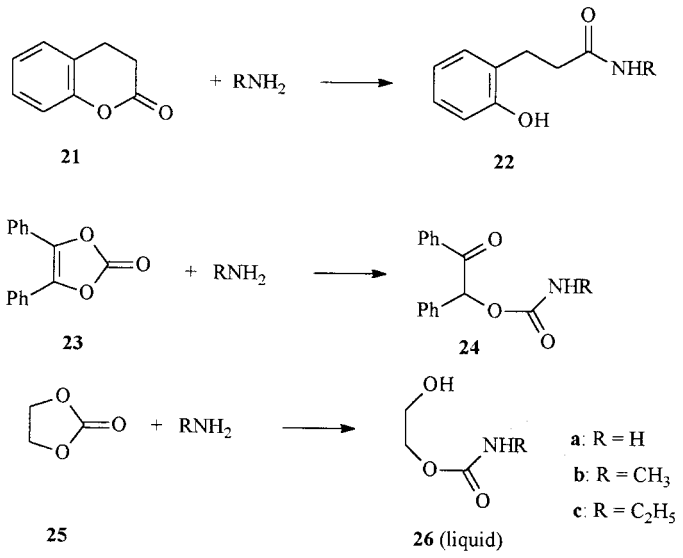


Figure 4. Molecular packing of **16a** on its (001)-face; the H-bridged dimers are highlighted by the drawing of the 2.118 Å H-bonds.



Scheme 5. Quantitative gas–solid ring opening of lactones or cyclic carbonates with gaseous amines.

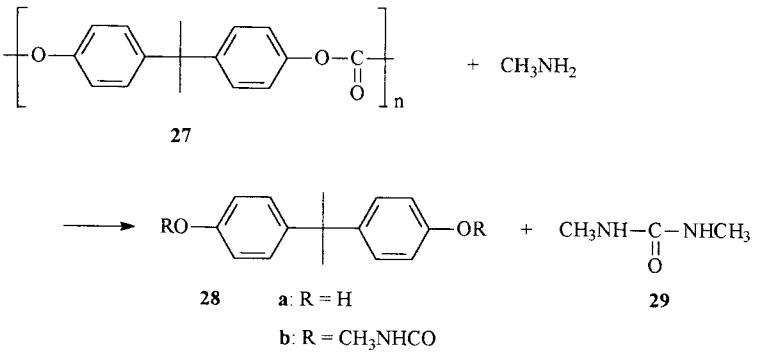
be sought in long-range anisotropic molecular movements within the reacting crystal.[1] The lack of submicromelting has been proven by an atomic force microscopy (AFM) investigation on a single crystal of **16a** with gaseous ethylamine. There is a direction of preference parallel to the long crystal axis in all stages of the reaction (Fig. 3a–d). The formation of heights seems to profit from the roughness on the surface, whereas the gradually formed craters orient themselves roughly orthogonal to the long axis and reach dephts of 20–50 nm (18–44 dimer layers). Later on, upon continuation of the reaction the heights and craters vanish (Fig. 3c) and finally heights and valleys along the long crystal axis are formed prior to disintegration. These highly anisotropic molecular movements in a 3-cascade reaction[16] are related to the crystal packing of **16a**.[17] Fig. 4 shows the molecular arrangement under the main (001)-surface.

The molecules form hydrogen-bridged pairs (dimers) which are inclined at 43°, form stacks along [100] and two dimensional infinite sheets parallel to (001). One half of the carbonyls are unbridged. Thus, there are glide planes between the dimer layers that facilitate the molecular movements upon chemical reaction of the amine which may approach the non-hydrogen-bridged carbonyl functions on the surface. Due to mass increase the molecules have to exit over the (001) surface. This happens irregularly, probably because there is faster reaction at rough surface parts. However, the craters that are left behind grow gradually along the stacking direction [100]. The direction of preference along [010] derives from a (101) glide plane that cuts (001) parallel to b at an angle of 80.5°. Thus, we have clear-cut correlations of the anisotropic movements to the crystal packing of **16a** that is maintained till the disintegration step.

Nucleophilic additions to lactones and carbonates

Solid lactones react with gaseous amines to give ring opened hydroxyamides. Typical examples are the reactions of dihydrocumarine **21** (mp 25°C) at 0°C or of diphenyldioxol-2-one **23** at 25°C that give 100% yield of the polyfunctional products **22a–c** and **24a–c** (after ketonization) (Scheme 5).

Similar reactions of solid ethylenecarbonate **25** (mp 39°C) yield liquid products **26a–c**. Thus, the yields are not quantitative though pretty good with 87–97%, because these latter transformations do not profit from the solid state benefits. Similar reactions in aqueous phase were reported to give yields of 95%.[18] The solid-state reactions are clearly superior and even ammonia gas reacts quantitatively and rapidly.



Scheme 6. Gas–solid aminolysis of polycarbonate Makrolone®.

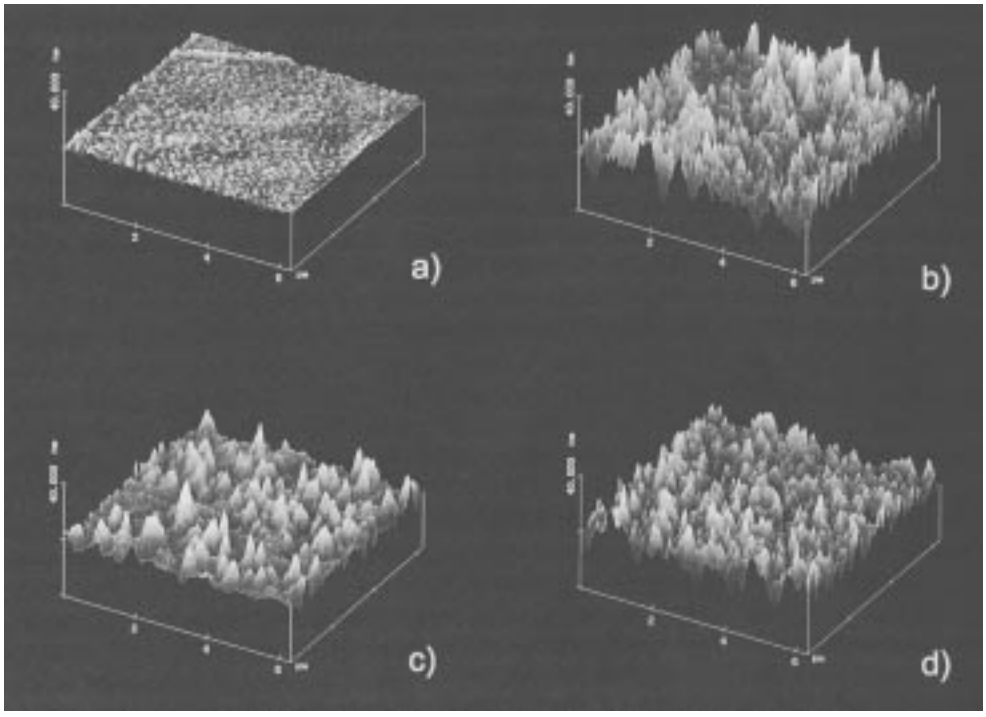


Figure 5. AFM topographies of PC **27** that was conditioned in clean wet air for some weeks: (a) untreated; (b) after 2 min application of CH_3NH_2 (1 bar); (c) after 1 min application of NH_3 (1 bar); (d) after 30 min application of NH_3.

The reactions of gaseous amines with the ester function are particularly efficient. Thus, it has been shown that ammonia and most efficiently methylamine gas aminolyze the thermoplastic polycarbonate Makrolon® (PC) **27** down to bisphenol A **28a** and dimethylurea **29**. Some bisurethane **28b** was also detected in the liquid that was rapidly obtained (Scheme 6).

Such degradation with ubiquitous gases has highest impact for the longterm stability of data-storage compact discs (CD) and was not reported before[19] when only aminolyses with liquids were known. It starts at the solid surface of the exposed polymer and was studied with AFM.[19] After the obvious recoiling of the polymer strands the surface became sticky and finally liquid (**28**+**29**; see Fig. 5).

The interaction of PC with ammonia gas was less efficient. After initial recoiling, the surface did not liquefy, probably because the surface developed a tight cover. Slow but continuous damage occurs also at exposed PC in amine containing ambient atmosphere. Such reaction decreases the lifetime of green houses or buildings with technical roofs out of PC. On the other hand the apparent possibilities for recycling of PC with gaseous methylamine appear to be uneconomic in view of the low prize of bisphenol A **28a**. Anyhow, lenses of PC need protecting coatings in order to decrease degradation by ambient gaseous amines.[19]

Cross-linked polycarbonates such as widely used CR 39 (poly-dialkyldiglycolcarbonate) are also degraded by gaseous methylamine.[19] The recoiling was also studied

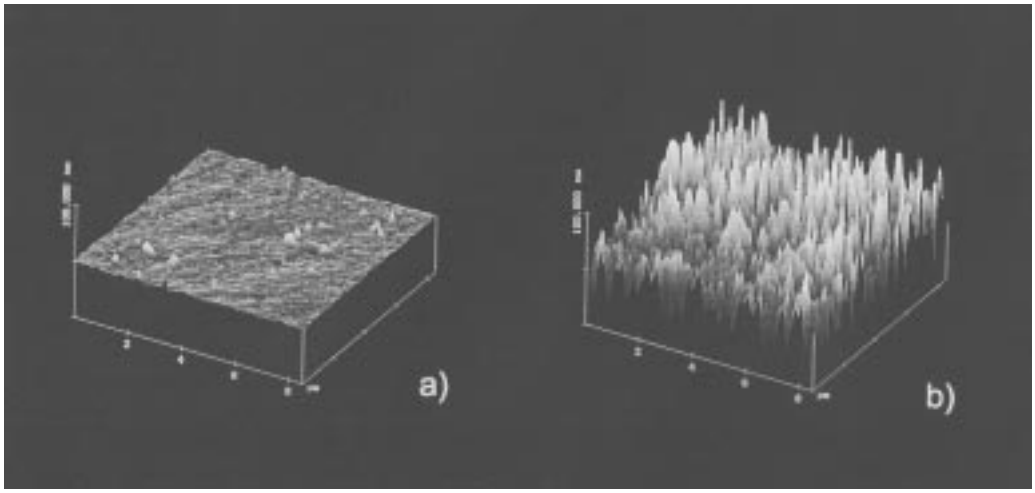
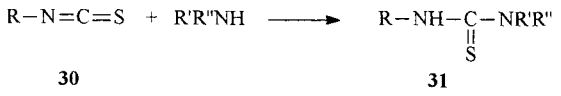


Figure 6. AFM topographies of CR 39 that was conditioned in clean wet air for some weeks: (a) before, (b) after 5 min treatment with CH_3NH_2 (1 bar).[19]

Table 2. Thioureas **31** from isothiocyanates **30** and amines

30	R	Mp (°C)	R′,R″	*p* (bar)	Temp. (°C)	Yield (%)	Mp (°C)	Lit. mp (°C)	Lit.
a	Ph	−21	H/H	0.4	−30	100	154	154	20
b	4-BrPh	60–61	Me/H	1	RT	100	60	60	21
c	4-BrPh	60–61	Me/Me	1	RT	100	163	163	22
d	1-Naph	56	Me/H	1	RT	100	197	198	23
e	1-Naph	56	Me/Me	1	RT	100	161	162	24
f	4-NO_2Ph	112–13	Me/H	1	RT	100	216	218	25
g	4-NO_2Ph	112–13	Me/Me	1	RT	100	182	176–177.5	26
h	Me	30	H/H	0.5	0	100	121	121	27
i	Me	30	Me/H	0.5	0	100	62	64	28
j	Me	30	Me/Me	0.5	0	100	88	87	29
k	Me	30	4-MeOPh/H		RT[a]	100	170	169	30
l	Me	30	4-Br-Ph/H		RT[a]	100	150	148	21
m	Me	30	4-Cl-Ph/H		RT[a]	100	149	147	31

[a] Intermediate softening or partial melting was observed.



Scheme 7. Quantitative gas–solid and solid–solid synthesis of thioureas from isothiocyanates and amines.

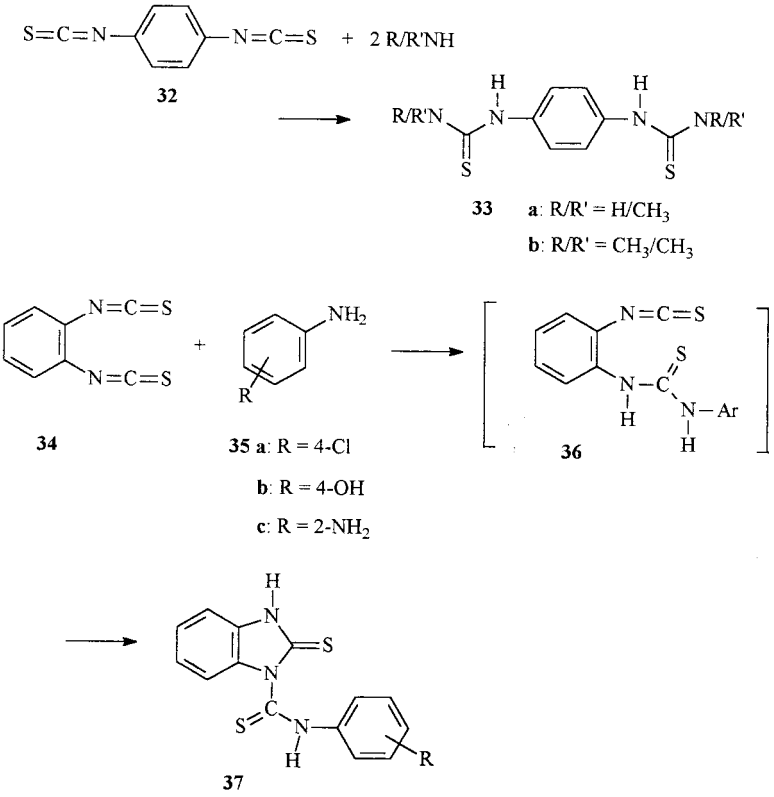
with AFM (see Fig. 6). Reaction started immediately and the surface became sticky. The damage of the surface was considerable at that stage (optical properties, mechanical stability, coatability). Thus, also cross-linked polycarbonate solid surfaces have to be protected from ambient deterioration by ubiquitous gaseous amines.

Interestingly, CR 39 surfaces were not changed after 1 h exposure to gaseous ammonia (1 bar), as was shown by the absence of significant recoiling at the surface when analyzing at the extreme sensitivity of the AFM.[19]

Additions to isothiocyanates

All studied solid isocyanates **30** gave quantitative yields of thioureas **31** when reacted with gaseous amines or solid anilines at suitable temperatures (see Table 2) (Scheme 7).

The solid-state techniques add to the value of this important path to thioureas, now without waste formation. Liquid phases are not involved in these gas–solid reactions. However, the solid–solid reactions of methylisothiocyanate with solid anilines (last three entries of Table 2) are so efficient that 100% yields of the crystalline arylthioureas



Scheme 8. Quantitative gas–solid and solid–solid synthesis of thioureas with bifunctional isothiocyanates.

were also obtained by grinding in a mortar, when intermediate melting occurred. In this case genuine solid-state transformations required low temperatures, an effort that could be avoided here. The high versatility of the quantitative thiourea syntheses has been extended to diisothiocyantes to give double and two-step reactions in the solid state (Scheme 8).

Thus, solid **32** reacts with gaseous methylamine or dimethylamine to give 100% yields in **33**, whereas solid **34** reacts with the solid amines **35** in a ball-mill at room temperature presumably via **36** to give 100% yields of **37**. Similar reactions in solution gave yields ranging from 81 to 95% and required workup.[32]

Conclusion

We report here 53 quantitative reactions with generally available materials to give useful products of wide application. Most of these reactions did not require any workup, four of them required washings but not recrystallisation or chromatography. Only 100% yield reactions may avoid wastes and are truly sustainable in terms of resources, energy and labor. Such favorable conditions are apparently bound to the solid-state and only the waste-free synthesis of **31k–m** tolerated a partial intermediate melting, while usually liquid-phase reactions do not provide 100% yield. It is essential that liquid phases be absent throughout the whole reaction, if 100% yield is desired. Numerous solid–solid reactions have been reported without observance of this requirement and thus the yields were often less than quantitative there.[33]

The purity of the starting materials is rarely better than 99%. Thus, the purity of the products in quantitative reactions without workup can not be better than that. The influence of impurities in that range is negligible to the melting points (some are higher than the reported ones) and everything stays in the detection limits of routine NMR. It appears that the three-step crystal mechanism leads more readily to completion of the reactions than the mechanism of similar liquid-phase reactions. While three conditions have to be fulfilled for the solid-state reactions to occur (phase rebuilding, phase transformation and crystal disintegration must run properly), they are always worth a try. The temperatures can be chosen lower than in liquid-state reactions due to higher reactivity. The extraordinary high selectivities derive from the crystal packings that are used in the anisotropic molecular movements. These are again shown in the Figs. 1 and 3. However, the supermicroscopic analysis by AFM provides additional information if solid-state reactions of polymers are probed, that show unusually rich solid-state reactivities.[19] AFM is a versatile means to detect the reasons for any nonreactivity if submicromelts occur, or if the mechanistic steps 2 or 3 do not proceed properly. Valuable hints for overcoming such obstacles[1] are obtained. Thus, the benefits of crystal reactions with gases or other crystals can be more often profited from. Only step 1 is totally governed by the crystal packing and cannot be influenced in a given system, unless polymorphs can be crystallized.

The upscaling is an important task for future use of solid-state reactions in waste-free chemical productions.[13] The 500 g run of **9** under laboratory conditions is promising in this respect in addition to the known kg scale solid-state syntheses with 100% yield.[1,13,34] The most important questions to be solved are aggregation, volume increase and heat transport, but technical solutions should not be out of reach, as fluidized bed reactors and large continuous mills are available. The versatility of the solid-state technique is clearly demonstrated again by the two-step trapping syntheses of **5** and **37**, by the double reaction of **6**, by the 3-cascade reactions of **16**, and the solid-state reaction sequence of **6** to **7** to **8**, that add to the previously reported complex reaction types. Furthermore, the reported reactions are well-suited for lab courses where both lecturers and students will enjoy to avoid solvents and liquid phases in order to achieve quantitative yields in their sustainable synthetic work.

Experimental

General methods

The starting materials were of good commercial quality and were but loosely ground or mostly used as obtained. Technical products were purified by proper recrystallization or distillation/sublimation. The moderately small crystals were not finely ground for the gas–solid reactions in order to avoid heavy reaction courses. Single crystals have been grown for the AFM measurements according to the literature procedures. Gases were taken from pressure or lecture bottles. The ball-mill was a Retsch MM2000 with a 10 mL stainless steal beaker and balls. It was run at 50 Hz (RT) or 25 Hz (cooling or heating). All solid-state reactions were first analyzed by FT-IR techniques (Perkin–Elmer 1720-X) in order to secure the progress of reaction. Only characteristic vibrations mostly in the double bond region are listed here. Yields were determined by weight, purity assessed by mp, ^{1}H NMR, and DC. All NMR spectra were taken at a Bruker WP 300 at 300 MHz (^{1}H) or 75 MHz (^{13}C). $CDCl_3$/DMSO-d_6 mixtures contained up to 10% DMSO-d_6. The AFM instrument was a Nanoscope® II (Digital Instruments). Symmetrically located, i.e. non-scraping tips were used throughout.[35] Further techniques have been reported elsewhere.[36]

Gas–solid reactions of aldehydes with amines to give 2 or 3

1.00 mmol of the crystalline aromatic aldehyde **1** were evacuated in a 50 mL round bottomed flask and treated with 1 bar of methyl- or ethylamine over night at room temperature. For **1b** 100 mL, 0.25 bar and 0°C were applied. Excess gas was condensed to a receiver at 77 K and the water of reaction removed from the crystals at 0.01 bar and 80°C. The purity of the weighed products was checked by mp and ^{1}H- and ^{13}C NMR.

The mps and vibration frequences of the C=N bonds are listed in Table 1. The spectra corresponded to the reported ones. **2a**: ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 3H),), 7.31–7.64 (AA′BB′, 4H), 8.19 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 48.0,

128.7, 128.9, 134.6, 136.3, 160.9. **3a**: ^{1}H NMR ($CDCl_3$) δ 1.32 (t, 3H), 3.71 (q, 2H), 7.38–7.69 (AA′BB′, 4H), 8.24 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.17, 55.77, 128.8, 129.2, 134.8, 136.4, 159.0. **3c**: ^{1}H NMR ($CDCl_3$) δ 1.31 (t, 3H), 2.97 (s, 6H), 3.58 (q, 2H), 6.63–7.63 (AA′BB′, 4H), 8.14 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.46, 40.04, 55.54, 111.51, 124.43, 129.23, 151.81, 160.25. **3d**: ^{1}H NMR ($CDCl_3$) δ 1.31 (t, 3H), 3.59 (q, 2H), 3.85 (s, 3H), 5.19 (s, 2H), 6.89 (m, 1H), 7.19–7.41 (m, 4H), 7.46–7.51 (m, 3H), 8.19 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.20, 55.40, 55.73, 70.65, 110.88, 111.23, 122.81, 127.32, 127.67, 128.28, 128.58, 128.98, 129.37, 136.67, 148.37, 151.63, 159.65; HRMS (CI, *i*-C_4H_{10}) *m/z* found 270.1386 calcd for $C_{17}H_{19}NO_2$ 270.1375 $(M+H)^+$

(*R*)-Thiazolidine-4-carboxylic acid 5. 242 mg (2.00 mmol) (L)-cysteine (**4**) and 62 mg (97%; 2.00 mmol) paraformaldehyde were ball-milled at room temperature for 1 h. After drying at 0.01 bar at 80°C, 263 mg (100%) of **5** were obtained; mp 196°C, lit. 196–197°C;[37] IR (KBr) cm^{-1} 3052, 2942, 2346, 1630, 1557, 1463, 1386; ^{1}H NMR (D_2O) δ 3.32 (mAB, 2H), 4.28 (m, 1H) 4.39 (m, 2H); ^{13}C NMR (D_2O) δ 33.32, 48.98, 64.31, 172.22.

Pyromellitic tetramethylamide 7. 436 mg (2.00 mmol) pyromellitic dianhydride **6** were evacuated in a 100 mL flask and treated overnight with 1 bar of gaseous methylamine. Excess gas was condensed in a separate flask at 77 K and 610 mg (100%) of **7** collected: mp 381°C; IR (KBr) cm^{-1} 3022, 1633, 1566, 1365; ^{1}H NMR (D_2O) δ 2.46 (s, 12H), 7.38 (s, 2H); ^{13}C NMR (D_2O) δ 24.78, 126.23, 138.12, 176.80.

Pyromellitic dimethylimide 8. 436 mg (2.00 mmol) of crystalline **6** were exposed to 0.8 bar methylamine as above and heated to 160°C overnight. Alternatively, 306 mg (1.00 mmol) **7** were heated to 160°C under vacuum with occasional evaporation. 485 mg (100%) or 245 mg (100%) of **8** were obtained. Alternatively, 306 mg **7** were treated with 1 bar of HCl at RT in an evacuated 100 mL flask over night, the excess gas condensed to a cooled flask (77 K), and methylamine hydrochloride washed away with water and the solid residue dried. The yield was 243 mg (100%); mp 381°C; lit. 375–378;[12] IR (KBr) cm^{-1} 3037, 1702, 1578; ^{1}H NMR ($CDCl_3$) δ 3.29 (s, 6H), 8.26 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 24.49, 118.14, 137.35, 166.25.

Ethyl-tetrachlorophthalamic acid, ethylammonium salt 10. Technical **9** was recrystallized from CCl_4. 572 mg (2.00 mmol) of the anhydride was evacuated in a 100 mL flask and left over night with 1 bar of ethylamine. Excess gas was recovered and 750 mg (100%) product **10** collected; mp 190°C; IR (KBr) cm^{-1} 3062, 1647, 1628, 1593; ^{1}H NMR (D_2O) δ 1.08 (t, 6H), 2.80 (q, 2H), 3.24 (q, 2H); MS (CI): 375–383 (M+1 with correct isotope pattern for $C_{12}H_{15}Cl_4N_2O_3$). 500 g of **9** were evacuated in a 2 L round bottomed flask on a rotatory evaporator. The setup was continuously filled with ethylamine (0.5–0.8 bar) from a steel bottle by adjusting a needle valve while using a security valve under a hood. The rotating flask was immersed in a cooling bath at about 14°C. When the heat production had ceased after 8 h the conversion was ca. 75% and became very slow, due to aggregation of the 40 μm grains into 0.5–3 mm particles.

The material was ground in a large mortar and afterwards reacted with ethylamine gas at 50°C for a quantitative yield. Clearly in technical runs large scale milling at suitable cooling should be performed.

***N*-(4-Tolyl)-phthalimid 11.** 296 mg (2.00 mmol) phthalic anhydride and 214 mg (2.00 mmol) 4-toluidine were ball-milled for 1 h and the product dried at 0.01 bar and 80°C, to give 507 mg (>99%) of product **11** mp 204°C; lit. 201–203°C;[38] IR (KBr) cm^{-1} 3461, 1715, 1514, 1465, 1383; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 7.32 (s, 4H), 7.76 (m, 2H), 7.92 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.14, 123.62(2C), 126.41(2C), 129.00, 129.72(2C), 131.82, 134.25(2C), 138.10, 167.35

Cyclic imides 12/13 and amines. Crystals of succinimide or glutarimide (200 mg, 2.02 or 1.77 mmol) were treated with 1 bar or 0.8 bar of methyl- or dimethyl- or ethylamine at RT or 80°C in a previously evacuated 500 mL flask and left overnight or for 8 h. Excess gas was recovered in a 77 K trap. The yield was quantitative in all cases.

***N*-Methyl-succinic diamide 14a.** Mp 160.5°C; lit. 159–161°C;[14a] IR (KBr) cm^{-1} 1649, 1570; ^{1}H NMR (D_2O) δ 2.40 (s, 3H), 2.62 (mc, 4H); ^{13}C NMR (D_2O) δ 26.1, 30.7, 31.1, 175.4, 177.9.

***N*-Ethyl-succinic diamide 14b.** Mp 178°C; lit. 176–178°C;[14b] IR (KBr) cm^{-1} 1642, 1558; ^{1}H NMR (D_2O), δ: 0.97 (t, 3H), 2.41 (mc, 4H), 3.15 (q, 2H); ^{13}C NMR (D_2O) δ 14.0, 30.4, 30.8, 33.4, 171.3, 174.1.

***N,N′*-Dimethyl-succinic diamide 14c.** Mp 189°C; lit. 192–193°C;[39] the mp did not increase by recrystallization from ethanol; IR (KBr) cm^{-1} 1695, 1630; ^{1}H NMR ($CDCl_3$) δ 2.55 (m, 2H), 2.65 (m, 2H), 2.93 (s, 3H), 3.01 (s, 3H), 5.58 (bp, 1NH), 6.41 (bp, 1NH); ^{13}C NMR ($CDCl_3$) δ 28.7, 30.7, 35.5, 37.0, 171.8, 175.1.

***N*-Methyl-glutaric diamide 15a.** Mp 128°C; IR (KBr) cm^{-1} 1645, 1548; ^{1}H NMR ($CDCl_3$/DMSO-d_6) δ 1.72 (m, 2H), 2.08 (m, 4H), 2.58 (d, 3H), 6.49 (bp, 1NH), 7.1 (bp, 1NH), 7.52 (bp, 1NH); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 21.3, 25.3, 34.5, 34.7, 172.4, 174.2; HRMS (CI, *i*-C_4H_{10}) *m/z* found 144.0900 calcd for $C_6H_{13}N_2O$ 144.0899 $(M+H)^+$.

***N*-Ethyl-glutaric diamide 15b.** Mp 133°C; IR (KBr) cm^{-1} 1647, 1546; ^{1}H NMR ($CDCl_3$/DMSO-d_6) δ 1.01 (t, 3H), 1.62 (m, 2H), 2.03 (m, 4H), 3.07 (q, 2H), 6.47 (bp, 1NH), 7.1 (bp, 1NH), 7.51 (bp, 1NH); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 14.5, 21.3, 33.3, 34.5, 34.9, 171.6, 174.3; HRMS (CI, *i*-C_4H_{10}) *m/z* found 158.1020 calcd for $C_7H_{15}N_2O$ 158.1055 $(M+H)^+$.

***N,N′*-Dimethyl-glutaric diamide 15c.** Mp 103°C; lit. 97–98°C;[39] IR (KBr) cm^{-1} 1683, 1618; ^{1}H NMR ($CDCl_3$/DMSO-d_6) δ 1.98 (m, 2H), 2.31 (m, 2H), 2.39 (m, 2H), 2.95 (d, 6H), 5.92 (bp, 1NH), 6.34 (bp, 1NH); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 20.8, 32.1, 34.9, 35.3, 172.5, 175.6;

HRMS (CI, *i*-C_4H_{10}) *m/z* found 158.1034 calcd for $C_7H_{15}N_2O$ 158.1055 $(M+H)^+$.

Phthalimides 16 and amines

2.00 mmol of the crystals **16a–c** were reacted overnight with methyl- or ethylamine (**16d** with ethylamine) in a pre-evacuated 500 mL flask. Excess gas was recovered in a separate flask at 77 K. The yields were quantitative in all cases. **16a** and methylamine were reacted at −20°C and 0.1 bar or with ethylamine at RT and 0.8 bar. **16b–d** were reacted with methyl- and ethylamine at RT and 0.8–1 bar. Glycine that was liberated from **16c** was washed away with water; the solid residue was dried in a vacuum.

***N,N′*-Dimethylphthalic diamide 19.** Mp 185°C; lit. 185°C;[14a] IR (KBr) cm^{-1} 1626, 1555; ^1H NMR (DMSO-d_6) δ 2.73 (d, 6H), 7.41 (AA′BB′, 4H), 8.15 (bp, 2NH).

***N,N′*-Diethylphthalic diamide 20.** Mp 169°C; lit. 162–163°C;[14a] IR (KBr) cm^{-1} 1644, 1590, 1568; ^1H NMR ($CDCl_3$) δ 1.21 (t, 6H), 3.38 (q, 4H), 6.88 bp, 2 NH), 7.40 (AA′BB′, 2H), 7.50 (BB′AA′, 2H).

Ring closure of diamides 19 and 20

A quantitative conversion of **19** or **20** (1.00 mmol) into **18** (R′=CH_3) or **16d** was obtained if HCl gas (RT, 1 bar) interacted overnight and if ethylammonium hydrochloride was washed away with water.

Equilibration of 20 and 19

Diamide **20** (1.0 mmol) was reacted with 0.8 bar of methylamine at RT for 18 h in a 100 mL flask. A 25:75 ratio of methyl (**19** and, probably, mixed diamide) and ethyl (**20** and mixed diamide) derivative was detected after evaporation of the gas. A similar run at 100°C gave a 42:58 ratio, respectively.

Gas–solid reactions of lactones

21 (2.00 mmol, 0°C, overnight), **23** (2.00 mmol, RT, 1 day), or **25** (7.5 mmol, RT, 1 h) were evacuated in 250 mL flasks and treated with 0.8 bar ammonia, methyl-, or ethylamine (**21** and ethylamine at 0.2 bar). Excess gas was recovered by condensation at 77 K. The products **22a–c** and **24a–c** formed quantitatively. The liquid products were isolated by distillation.

3-(2-Hydroxyphenyl)-propionamide 22a. 100% yield; mp 89°C; lit. 89.5–90°C;[40] IR (KBr) cm^{-1} 3368, 1671, 1619, 1605; ^1H NMR ($CDCl_3$) δ 2.67 (t, 2H), 2.86 (t, 2H), 5.55 (bp, 2 NH), 6.9 (m, 2H),7.12 (m, 2H).

Methyl-3-(2-hydroxyphenyl)-propionamide 22b. 100% yield; mp 170–171°C; IR (KBr) cm^{-1} 3294, 3172, 1624, 1588; ^1H NMR ($CDCl_3$), δ: 2.61 (t, 2H), 2.80 (d, 3H), 2.92 (t, 2H), 6.81 (t, 1H), 6.88 (d, 1H), 7.05 (m, 2H); $C_{10}H_{13}NO_2$ (179.22) found C 67.11, H 7.35, N 7.93; calcd C 67.02, H 7.31, N 7.82.

Ethyl-3-(2-hydroxyphenyl)-propionamid 22c. 100% yield; mp 111°C; IR (KBr) cm^{-1} 3287, 3181, 1618, 1603, 1569; ^1H NMR ($CDCl_3$) δ 1.06 (t, 3H), 2.56 (t, 2H), 2.91 (t, 2H), 3.23 (q, 2H), 6.80 (t, 1H), 6.88 (d, 1H), 7.06 (m, 2H); $C_{11}H_{15}NO_2$ (193.24) found C 68.29, H 7.96, N 7.36; calcd C 68.37, H 7.82, N 7.36.

Carbamic 1-phenylphenacylester[41] 24a. 100% yield; mp 206°C; IR (KBr) cm^{-1} 1751; ^1H NMR ($CDCl_3$) δ 7.20 (m, 2H), 7.28 (m, 2H), 7.43 (m, 3H), 7.54 (m, 4H).

Methylcarbamic 1-phenylphenacylester 24b. 100% yield; mp 204°C; IR (KBr) cm^{-1} 1750; ^1H NMR ($CDCl_3$) δ 2.77 (s, 3H), 7.20 (m, 2H), 7.40 (m, 3H), 7.47 (m, 5H); $C_{16}H_{15}NO_3$: found C 71.35, H 5.70, N 5.32; calcd C 71.36, H 5.61, N 5.20.

Ethylcarbamic 1-phenylphenacylester 24c. 100% yield; mp. 186°C; IR (KBr) cm^{-1} 3408, 1748; ^1H NMR ($CDCl_3$) δ 1.13 (t, 3H), 3.17 (q, 2H), 7. 20 (m, 2H), 7.26 (m, 2H), 7.39 (m, 2H), 7.49 (m, 3H); $C_{17}H_{17}NO_3$: found C 71.87, H 5.97, N 5.14; calcd C 72.07, H 6.05, N 4.98.

Gas–solid reaction of 1,3-dioxolane-2-one 25 with gaseous amines

7.5 mmol of **25** was exposed to 1 bar of the gaseous amine in a 500 mL flask for 1 h. The liquid product **26** was purified by distillation.

Carbamic 2-hydroxyethylester 26a. 92% yield; bp_{17} 208–210°C; lit. 300°C;[18] IR (KBr) cm^{-1} 1699; ^1H NMR (D_2O) δ 3.66 (m, 2H), 4.0 (m, 2H).

Methylcarbamic 2-hydroxyethylester 26b. 93% yield; bp_{17} 177°C; lit. 270°C;[18] IR (KBr) cm^{-1} 1699, 1539; ^1H NMR (D_2O) δ 2.64 (s, 3H), 3.64 (m, 2H), 4.03 (m, 2H).

Ethylcarbamic 2-hydroxyethylester 26c. 92% yield; bp_{17} 154°C; lit. 153–154°C;[18] IR (KBr) cm^{-1} 1699, 1539; ^1H NMR (D_2O) δ 1.0 (t, 3H), 3.03 (q, 2H), 3.63 (m, 2H), 4.0 (m, 2H).

Reaction of injection molded polymers with amines

The polymer surfaces of PC (Makrolon®) or CR 39 were exposed for several weeks to clean moist air.[19] After initial AFM measurement,[19] the basic gases were applied with a syringe directly on the AFM stage from about 1 mm distance and blown away after 1 min. AFM images were stable for 5–10 scans (see Figs. 5 and 6).

Solid-state reactions of isothiocyanates with amines

Crystalline isothiocyanates **30**, **32** (Aldrich), or **34** (lit.[32]) (2.00 mmol; 250 mL flask; overnight) were, depending on the mps and eutectica, reacted with the basic gases or with the solid anilines (2.00 mmol) in a mortar(occasional grinding and standing for 1 day), as indicated in Table 2. Excess

gases were recovered by condensation at 77 K. The yields were 100% in all cases.

***N*-Phenylthiourea 31a.** IR (KBr) cm^{-1} 1613, 1590, 1522; ^1H NMR (D_2O) δ 7.21 (m, 2H), 7.28 (m, 1H), 7.4 (m, 2H).

1-(4-Bromophenyl)-3-methyl-thiourea 31b. IR (KBr) cm^{-1} 1726, 1616, 1594, 1558; ^1H NMR ($CDCl_3$) δ 3.15 (s, 3H), 7.18 (AA′BB′, 2H), 7.5 (BB′AA′, 2H).

3-(4-Bromophenyl)-1,1-dimethyl-thiourea 31c. IR (KBr) cm^{-1} 1642, 1587, 1539; ^1H NMR ($CDCl_3$) δ 3.38 (s, 6H), 7.18 (AA′BB′, 2H), 7.43 (BB′AA′, 2H).

1-Methyl-3-naphthalene-1-yl-thiourea 31d. IR (KBr) cm^{-1} 1632, 1540, 1513; ^1H NMR ($CDCl_3$) δ 3.09 (s, 3H), 7.40–7.61 (m, 4H), 7.80–8.05 (m, 3H).

1,1-Dimethyl-3-naphthalene-1-yl-thiourea 31e. IR (KBr) cm^{-1} 1536; ^1H NMR ($CDCl_3$) δ 3.31 (s, 6H), 7.22–7.56 (m, 4H), 7.72–8.00 (m, 3H).

1-(4-Nitrophenyl)-3-methyl-thiourea 31f. IR (KBr) cm^{-1} 1617, 1504; ^1H NMR ($CDCl_3$) δ 3.30 (s, 3H), 7.38 (AA′BB′, 2H), 8.24 (BB′AA′, 2H).

3-(4-Nitrophenyl)-1,1-dimethyl-thiourea 31g. IR (KBr) cm^{-1} 1604, 1547, 1513; ^1H NMR ($CDCl_3$) δ 3.41 (s, 6H), 7.46 (AA′BB′, 2H), 8.20 (BB′AA′, 2H).

1-Methyl-thiourea 31h. IR (KBr) cm^{-1} 1632, 1555; ^1H NMR (DMSO-d_6) δ 2.79 (s, 3H), 7.52 (bp, 2NH).

1,3-Dimethyl-thiourea 31i. IR (KBr) cm^{-1} 1565, 1505; ^1H NMR (DMSO-d_6) δ 3.04 (d, 6H), 7.50 (bp, 2NH).

1,1,3-Trimethyl-thiourea 31j. IR (KBr) cm^{-1} 1557; ^1H NMR ($CDCl_3$) δ 2.95 (d, 3H), 3.11 (s, 6H).

1-(4-Methoxyphenyl)-3-methyl-thiourea 31k. IR (KBr) cm^{-1} 1606, 1517; ^1H NMR ($CDCl_3$) δ 2.98 (s, 1NH), 3.08 (s, 3H), 3.81 (s, 3H), 6.90 (AA′BB′, 2H), 7.21 (BB′AA′, 2H), 8.86 (bp, 1NH).

1-(4-Bromophenyl)-3-methyl-thiourea 31l. IR (KBr) cm^{-1} 3268, 1599, 1557, 1486, 1381; ^1H NMR ($CDCl_3$/DMSO-d_6) δ 3.02 (d, 3H), 3.15 (bp, 1 NH), 7.3–7.5 (AA′BB′, 4H), 9.30 (bp, 1NH).

1-(4-Chloro-phenyl)-3-methyl-thiourea 31m. IR (KBr) cm^{-1} 1616, 1558; ^1H NMR ($CDCl_3$/DMSO-d_6) δ 3.02 (d, 3H), 3.18 (bp, 1NH), 7.27 (AA′BB′ 2H), 7.41 (BB′AA′, 2H), 9.21 (bp, 1NH).

1-Methyl-3-[4-(3-methyl-thioureido)-phenyl]-thiourea 33a. *p*-Phenylen-di-isothiocyanate (500 mg, 2.60 mmol) were reacted overnight with methylamine (1 bar; 500 mL; RT) to give 660 mg (100%) of **33a** after condensation of excess gas at 77 K. Mp 243°C; IR (KBr) cm^{-1} 1556; ^1H NMR (DMSO-d_6) δ 2.83 (d, 6H), 7.28 (s, 4H), 7.58 (bp, 2NH), 9.45 (bp, 2NH); $C_{10}H_{14}N_4S_2$ (254.37) found C 47.08, H 5.79, N 21.91; calcd C 47.22, H 5.55, N 22.03.

3-[4-(3,3-Dimethyl-thioureido)-phenyl]-1,1-dimethyl-thiourea 33b. *p*-Phenylen-di-isothiocyanate (500 mg, 2.60 mmol) were reacted overnight with dimethylamine (1 bar, 500 mL, RT) to give 730 mg (100%) of **33b** after condensation of excess gas at 77 K. Mp 258°C; lit. 253–254;[42] IR (KBr) cm^{-1} 1546, 1519; ^1H NMR (DMSO-d_6) δ 3.27 (s, 12H), 7.20 (s, 4H), 8.81 (bp, 2NH).

1-(4-Chloranilino-thiocarbonyl)-benzimidazolidine-2-thione[32] 37a. 255 mg (2.00 mmol) 4-chloroaniline and 384 mg (2.00 mmol) *o*-phenylene-di-isothiocyanate were ball-milled for 1 h to give 640 mg (100%) **37a**; mp 176°C; IR (KBr) cm^{-1} 1529; ^1H NMR ($CDCl_3$/DMSO-d_6) δ 7.20 (m, 3H), 7.39 (AA′BB′, 2H), 7.54 (m, 1H), 8.01 (BB′AA′, 2H); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 108.55, 110.18, 121.20, 122.43, 122.74, 127.27 (2C), 130.09, 130.88, 135.77, 165.88, 172.63.

1-(4-Hydroxyanilino-thiocarbonyl)-benzimidazolidine-2-thione 37b. 218 mg (2.00 mmol) *p*-hydroxyaniline and 384 mg (2.00 mmol) *o*-phenylene-di-isothiocyanate were ball-milled for 1 h to give 600 mg (100%) **37b**; mp 177°C; lit. 177–178°C;[32] IR (KBr) cm^{-1} 1602, 1553, 1509; ^1H NMR ($CDCl_3$/DMSO-d_6) decomposition.

1-(2-Aminoanilino-thiocarbonyl)-benzimidazolidine-2-thione[32] 37c. 216 mg (2.00 mmol) *o*-phenylenediamine and 384 mg (2.00 mmol) *o*-phenylene-di-isothiocyanate were ball-milled for 1 h to give 595 mg (100%) **37c**; mp.: 109°C; IR (KBr) cm^{-1} 1620, 1504; ^1H NMR ($CDCl_3$/DMSO-d_6) decomposition.

Supplementary Material

The submicroscopic changes of PC (Makrolon®) and of cross-linked CR 39 upon exposure to methylamine or ammonia gas were studied by AFM.[19]

The AFM image of injection molded PC (Makrolon®) shows a very flat (R_{ms}=0.48 nm) surface (Fig. 5a). Efficient recoiling is seen in Fig. 5b (R_{ms}=4.24 nm) after 2 min exposure to methylamine gas. Further exposure led to softening and finally liquefying of the surface.

Also the recoiling of a fresh sample of PC with ammonia gas (c,d) started immediately. The roughness in c is R_{ms}= 2.29 nm after 1 min exposure and 3.34 nm after 30 min exposure in (d). Further reaction with ammonia was very slow and liquefying is not observed. The recoiling of cross-linked polycarbonate CR 39 (poly-dialkyldiglycolcarbonate) by interaction of gaseous methylamine is shown in the AFM images of Fig. 6.

A rather flat initial surface (R_{ms}=1.2 nm) formed solid structures (R_{ms}=22 nm) after 5 min exposure. Further reaction (15 min) decreased the features (R_{ms}=12 nm) and the surface became sticky.

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References

1. Kaupp, G. *Supermicroscopy in Supramolecular Chemistry: AFM, SNOM, and SXM*; In *Comprehensive Supramolecular Chemistry*, Davies, J. E. D. Ed.; Elsevier: Oxford, 1996; Vol. 8, pp 381–423 (21 color plates).
2. Schmeyers, J.; Toda, F.; Boy, J.; Kaupp, G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 989–993.
3. Pitra, D.; Grasso, D.; Farini, G. *J. Mol. Struct.* **1971**, *10*, 101–110.
4. Baddar, F. G. *J. Chem. Soc.* **1950**, 136–139.
5. Cromwell, N. H.; Hoeksma, H. *J. Am. Chem. Soc.* **1949**, *67*, 1658–1660.
6. Elias, H.; Froehn, U.; von Irmer, A.; Wannowins, K. J. *J. Inorg. Chem.* **1980**, *19*, 869–876; Zuchi, G.; Mavrodin, A. *Rev. Chim. (Bucharest)* **1975**, *26*, 986–988; *Chem. Abstr.* **1976**, *85*, 21539c.
7. Vanderlaan, D. G.; Schwartz, M. A. *J. Org. Chem.* **1985**, *50*, 743–748.
8. Björgo, J.; Boyd, D. R.; Watson, C. G.; Jennings, W. B.; Jerina, D. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1081–1084.
9. Iwasaki, F. *Acta Crystallogr. B* **1977**, *33*, 1646–1648.
10. Kaupp, G.; Schmeyers, J.; Boy, J. *J. Prakt. Chem.* **2000**, *342*, 269–280.
11. Miller, R. S.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5117–5119.
12. Cobb, R. L.; Mahan, J. E. *J. Org. Chem.* **1977**, *42*, 2829–2832.
13. Kaupp, G.; Schmeyers, J.; Boy, J. Waste-free solid-state syntheses with quantitative yield. *Chemosphere* **2000**, in press.
14. (a) Spring, S.; Woods, J. C. *J. Chem. Soc.* **1945**, 625–628. (b) Mizuno, S.; Hirata, Y. *Nagoya Kogyo Daigako Jakuho* **1959**, *11*, 241–245; Chem. Abstr. **1950**, *55*, 17260c.
15. Pifferi, G.; Fontanella, L.; Occelli, E.; Monguzzi, R. *J. Heterocycl. Chem.* **1972**, *9*, 1209–1214.
16. Kaupp, G.; Schmeyers, J.; Kuse, A.; Atfeh, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2896–2899.
17. Ng, S. W. *Acta Crystallogr. C* **1992**, *48*, 1195–1694.
18. Delaby, R.; Sekera, P.; Chabrier, P.; Piganiol, P. *Bull. Soc. Chim. Fr.* **1951**, *18*, 392–397.
19. Kaupp, G.; Schmeyers, J.; Haak, M.; Marquardt, T.; Plagmann, M.; Juniel/Kramer, M. Erforschung von Systemlösungen für transparente Verschleißschutzschichten auf Kunststoffen für die Optik, organische Haftvermittlungsschichten mit kovalenter Anbindung/Exploration of comprehensive answers for the problem of transparent wear-protective coatings on plastic materials for the optical industry, organic coatings and organic adhesion mediator coatings with covalent bonding; *BMBF Research Report* 13N6250; February 1997; pp 1–63.
20. Burkhardt, J. *Chem. Ber.* **1970**, *103*, 1589–1598.
21. Hunter, R. F.; Soyka, C. *J. Chem. Soc.* **1926**, 2958–2964.
22. Hunter, R. F.; Desai, R. D.; Buksh, M. W. *J. Indian Chem. Soc.* **1934**, *11*, 863–866.
23. Dyson, G. M.; Hunter, R. F. *Recl. Trav. Chim. Pays-Bas* **1926**, *45*, 421–423.
24. Hunter, R. F.; Styles, E. R. *J. Chem. Soc.* **1927**, 1209–1213.
25. Hunter, R. F.; Parken, E. R. *J. Chem. Soc.* **1935**, 1755–1761.
26. Isaksson, G.; Sandstroem, J. *Acta Chem. Scand.* **1970**, *24*, 2565–2582.
27. Sahasrabudhey, R. H.; Singh, R. *J. Indian Chem. Soc.* **1953**, *30*, 499–501.
28. Shaw, W. H. R.; Walker, D. G. *J. Am. Chem. Soc.* **1957**, *79*, 3683–3686.
29. Lecher, H.; Graf, F. *Chem. Ber.* **1923**, *56*, 1326–1330.
30. King, H.; Tonkin, I. M. *J. Chem. Soc.* **1946**, 1063–1069.
31. Hunter, R. F.; Jones, W. *J. Chem. Soc.* **1930**, 2190–2193.
32. Griffiths, D.; Hull, R.; Seden, T. P. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1240–1244.
33. Toda, F. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Ed.; Elsevier, Oxford, 1996; Vol. 6, pp 465–516; Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025–1074.
34. Kaupp, G., *Chemie unserer Zeit* **1997**, *31*, 129–139; Engl. transl. in http://kaupp.chemie.uni-oldenburg.de.
35. Kaupp, G.; Plagmann, M. *J. Photochem. Photobiol. A. Chem.* **1994**, *80*, 399–407; Kaupp, G.; Schmeyers, J.; Pogodda, U.; Haak, M.; Marquardt, T.; Plagmann, M. *Thin Solid Films* **1995**, *264*, 205–211.
36. Kaupp, G.; Schmeyers, J.; Boy, J. *Chem. Eur. J.* **1998**, *4*, 2467–2474; Kaupp, G.; Pogodda, U.; Schmeyers, J. *Chem. Ber.* **1994**, *127*, 2249–2261; Kaupp, G.; Schmeyers, J. *J. Org. Chem.* **1995**, *60*, 5494–5503; Kaupp, G.; Boy, J.; Schmeyers, J. *J. Prakt. Chem./Chem.-Ztg.* **1998**, *340*, 346–355.
37. Ratner, S.; Clarke, H. T. *J. Am. Chem. Soc.* **1937**, *59*, 200–206.
38. Lopez-Alvarado, P.; Avendano, C.; Menendez, J. C. *J. Org. Chem.* **1996**, *61*, 5865–5870.
39. Gellmann, S. H.; Dado, G. P.; Liang, G.-B.; Adams, B. R. *J. Am. Chem. Soc.* **1991**, *113*, 1164–1173.
40. Zagorevskij, V. A.; Savel'ev, V. L.; Dudykina, N. V. *J. Org. Chem. USSR (Engl. Transl.)* **1968**, *4*, 1970–1977; *Zh. Org. Khim.* **1968**, *4*, 2041–2048; *Chem. Abstr.* **1969**, *70*, 28767z.
41. Lohmann, D.; D'Hondt, C. *ACS Symp. Ser.* **1987**, *371*, 208–221; *Chem. Abstr.* **1988**, *109*, 124276z.
42. Landquist, J. K. *J. Chem. Soc., C* **1967**, 2212–2220.