Iminium Salts in Solid-State Syntheses Giving 100% Yield [1])

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Abstract. Numerous reaction types in the field of iminium salts are performed in the gas-solid and solid-solid techniques in order to reach 100% yield. The stoichiometric runs are waste-free and do not require costly workup. Frequently, iminium salts were avoided, as acid catalysis was dispensable. Thioureas and α-halogenated ketones give a variety of 2-aminothiazoles *via* thiuronium salts in quantitative yield. A new intramolecular solid-state thermal condensation is reported. Enaminoketones are synthesized quantitatively from anilines and 1,3-diketones without catalysis and those can be used for quantitative solid-state 4-cascade reactions. Solid paraformaldehyde is used to produce methylene imines and internally trapped methylene iminium salts. Benzoylhydrazones are produced again without catalysis in the solid state. Vacuum and ball-mill techniques are particularly useful in the production of highly sensitive iminium salts. Hexahydro-1,3,5-triazines cyclorevert upon exposure to HCl gas to give solid arylmethylene iminium chlorides as new versatile reagents. These are used in arylaminomethylations of β-naphthol and of themselves to give Troeger's bases in 3-cascades. More direct are 4-cascade Troeger's base syntheses by dissolving hexahydro-1,3,5-triaryltriazines in trifluoroacetic acid. Alkylations of imines with trimethyloxonium tetrafluoroborate and triphenylmethyl cation give highly sensitive quaternary iminium salts in the ball-mill. The products are characterized by spectroscopic techniques and density functional theory (DFT) calculations at the B3LYP 6-31G* level. Molecular movements in the crystal and surface passivation are investigated with atomic force microscopy (AFM) techniques.

Organic reactions that give 100% yield and do not require workup are environmentally benign and particularly versatile. Their use should also be considered if highly sensitive reagents and products are involved. Indeed, waste-free reactions occur frequently in solid-state iminium salt chemistry [1]. Mechanistic knowledge from supermicroscopic investigations (AFM and SNOM) verify three-step mechanisms that consist of phase rebuilding, phase transformation and crystal disintegration in solid-state reactions without liquid phase and far-reaching anisotropic molecular movements. It is thus comprehensible that gas-solid and solid-solid reactions tend to be complete and selective with the aid of crystal packing effects. It is essential that mechanical treatment (grinding, milling, ultrasound) reestablish fresh contacts of reacting crystals over and over again for the completion of solid-solid reactions to occur [2]. Anyhow, solid-state reactions have not yet been included in organic textbooks despite repeated reports on their environmental benefits and their superior practicability due to the avoidance of work-up and wastes [3, 4, 5]. Anyhow, many published examples using commonly available reagents in stoichiometric quantities would deserve such inclusion, because they are particularly easy, save work and energy and are just better, if they give 100% yield without workup. Even liquids can be solidified in various instances by cooling or complexation or salt formation and that extends the scope of solid-state reactions in a useful way. Thus, broad applications of organic solid-state syntheses might be foreseen and they will certainly succeed despite some historic reservations against them. We report here on numerous diverse reactions in iminium salt chemistry in six chapters, in order to promote such developments.

1. 2-Aminothiazoles and Thiuronium Salts

Thioureas **1** are easily accessible and frequently used in the synthesis of heterocyclic compounds [6]. Their reaction with phenacyl bromide **2** gives biologically active 2-amino-4-phenyl-thiazole-hydrobromides **3** in 80–90% yields in solution [7]. In the absence of solvent and liquid phase we obtain quantitative yields in numerous cases from stoichiometric mixtures of the reagents at room temperature. The water of reaction does not hydrolyze **2** under our mild conditions. If the reactants **1** and **2** are ball-milled in the ratio of 1:1 a quantitative yield of **3** is obtained. The water of reaction is removed from **3** at 80 °C *in vacuo*. If the same reaction of **1a**–**c** was performed in a melt at 110 °C some hydrolysis of **2** (ca. 5%) occurred; the yield was lowered and workup would be required. These quantitative solid-state heterocyclic syntheses are highly versatile. It is

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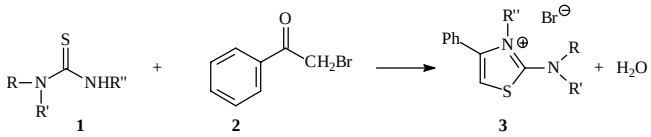
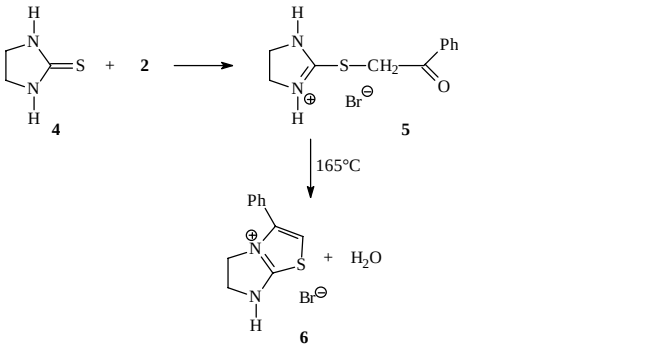


1 **2** **3**

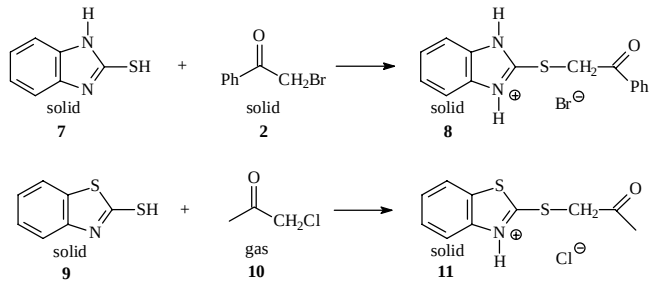
a: R = R' = R" = H
b: R = CH_3, R' = R" = H
c: R = R' = C_6H_5, R" = H
d: R = CH_3, R' = H, R" = CH_3
e: R = C_6H_5, R' = H, R" = C_6H_5
f: R = 4-ClC_6H_4, R' = H, R" = CH_3
g: R = R' = R" = CH_3

not required that the thiourea component contain a primary amino group as in **1a**–**c**. Thus, compounds **3d**–**g** are obtained with 100% yield from the corresponding *N*,*N'*-substituted thioureas and **2** when ball-milled in a 1:1 ratio. The orientation selectivity to give the products **3b** and **3f** points to the expected intermediacy of thiuronium salts that cyclize with the more nucleophilic amino groups of **1b** and **1f**. In the case of **4** the thiuronium salt **5** is isolated in quantitative yield. The interesting heterocycle **6** [8] is obtained therefrom in a solid-state intramolecular condensation reaction with 100% yield by heating to 165 °C.



4 **5** **6**

Further thiuronium salts are quantitatively obtained if solid 2-mercaptobenzimidazole (**7**) is ball-milled with solid **2** or 2-mercaptobenzothiazole (**9**) is reacted with chloroacetone (**10**) vapor.



7 **2** **8**

9 **10** **11**

On the other hand, similar reactions in solution are incomplete and generate corrosive wastes. It appears that both the solid-state synthesis of thiuronium salts and their cyclization to give various 2-aminothiazoles may find widespread application because they can be run „waste-free“.

The two-step solid-state reaction **1** + **2** –> **3** was probed on the (001)-face of thiourea **1a** with tiny crystallites (weight: ca.150 µg) of phenacylbromide **2** on it in 0.5 mm distance from the contact edge in *a*-direction. Far-reaching molecular movements are evident from Figure 1. The initially rather smooth surface becomes rough (R_{ms} = 5.59 nm, max height 42.7 nm) and 723 isolated volcanoes between shallow craters are depicted in Figure 1b. The surface changes rapidly to give mountain-chains and deep valleys with some directional preference in the *x*- (*a*-) direction (R_{ms} = 14.69 nm, max height 80.7 nm in Figure 1c). At that stage peaks and depths are of same height (an inverted image upside down has the same appearance). Finally, the roughness is leveled (Figure 1d).

The AFM images prove the absence of liquid phases [3, 4]. The sequence of events is reminiscent of erosion processes on geological objects when valleys and side valleys form and become deeper and wider and finally level. It was shown by tlc evidence that the molecules **1a** migrate through the contact interfaces into the crystal of **2**. Thus, the changes that are seen on the surface of the **1a**-crystal are indeed the result of withdrawal of molecules, but not of product formation, which occurs in the crystal of **2**. The anisotropy of the molecular movements must correlate to the crystal packing, of course.

The crystal packing in Figure 2 shows the molecules of thiourea forming H-bridged strands that are vertical under (100). Every molecule forms four hydrogen bonds (2.574 Å) in nearly planar 8-membered rings. Further intermolecular distances are larger than the van der Waals distances (S···H >2.730 Å; N···H >3.027 Å). The chemically productive movements in the experiment of Figure 1 are above the (001)-surface through the interface in the contact region. Hydrogen bridges have to be given up and the remaining gaps must be filled by drain from the sides, both from the bulk and from the surface region. Migration in *a*-direction parallel to (010) appears easier than a more zigzag movement in *b*-direction which is responsible for the side valleys. The drain of molecules initially leaves behind the isolated hills. The valleys have a tendency for the *a*-direction and they become deeper and wider, and finally the surface levels. Thus, a correlation to the crystal packing is clearly present. These submicroscopic events (due to molecular movements in the crystal) were observed at the remarkably large distance of 0.5 mm from the contact edge and again support the new mechanism of solid-state reactions [3, 4, 5].

2. Enamine Ketones

Solid 1,3-dicarbonyl compounds **12** such as 1,3-cyclo-

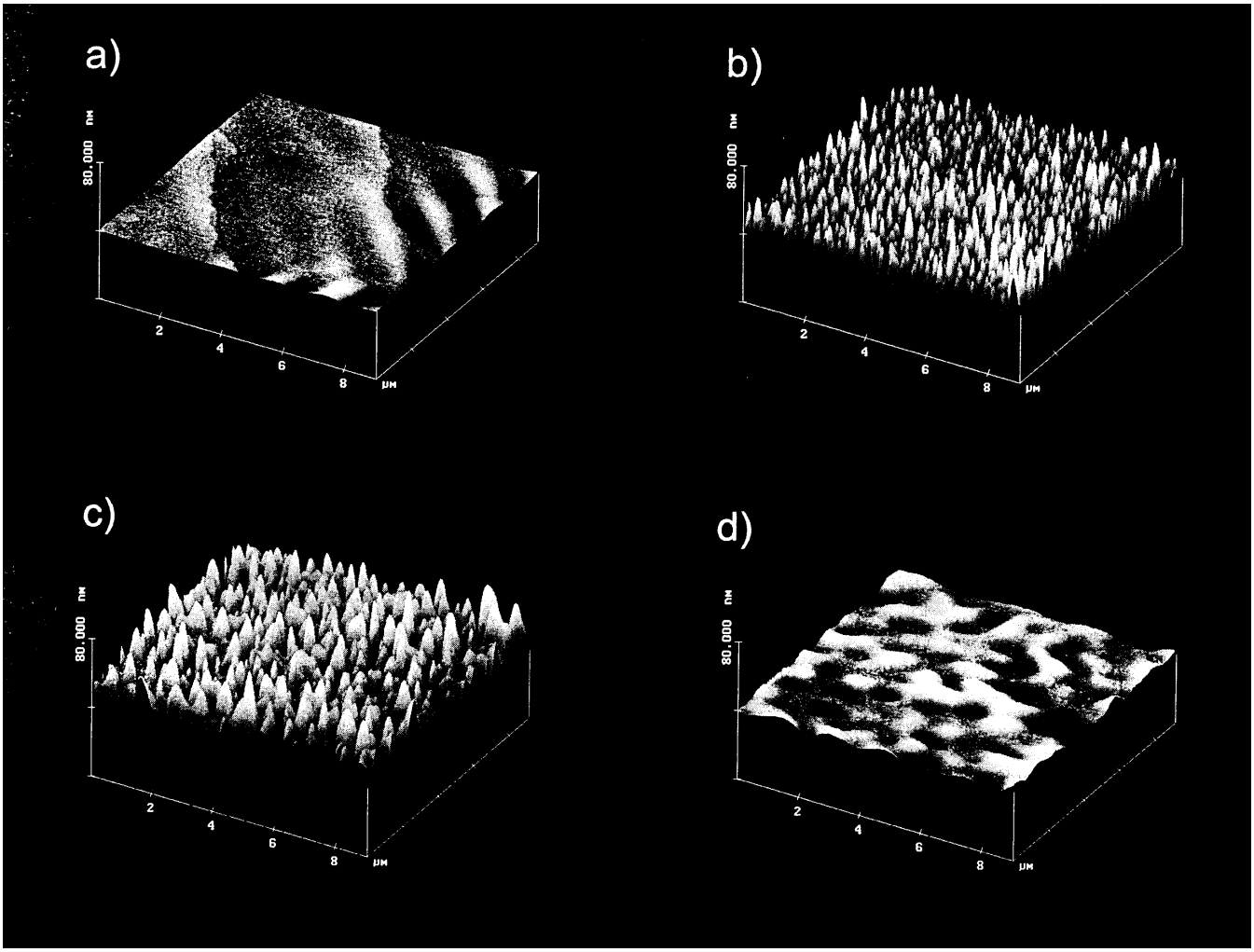


Fig. 1 9 µm AFM topographies on (001) of thiourea (Pbnm) [9] with tiny (150 µg) crystallites of phenacylbromide on top at 0.5 mm distance from the contact edge; a) fresh; b) after 4 min; c) after 11 min; d) after 53 min reaction; the molecules **1a** moved from right to left; tip and crystallite were aligned in the *a*-direction of the crystal.

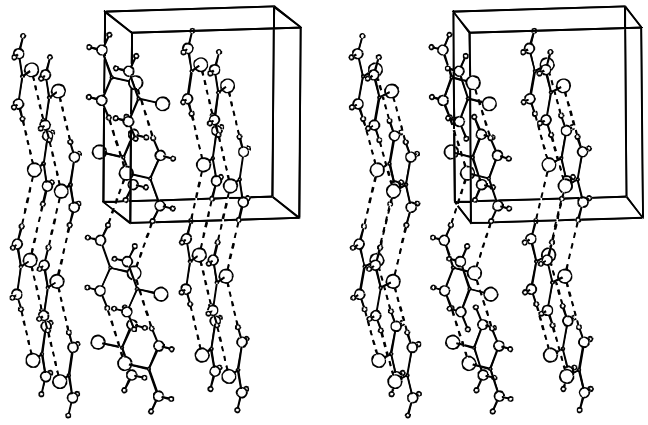
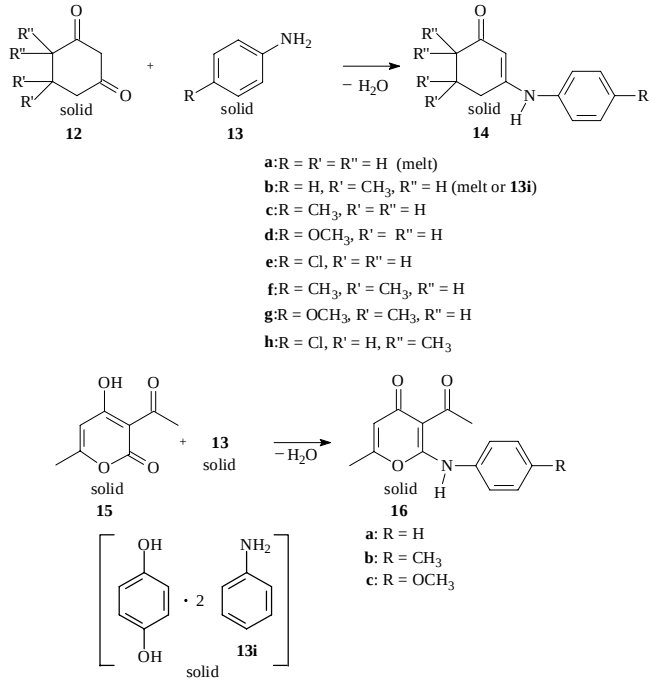


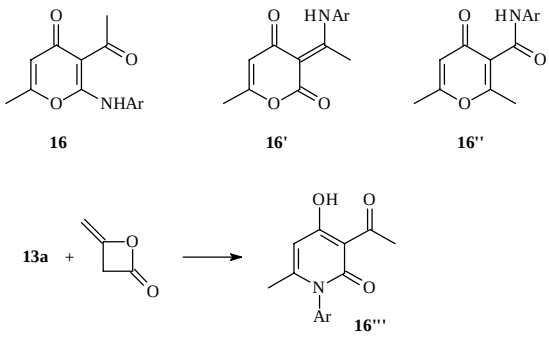
Fig. 2 Stereoscopic view of the crystal packing of thiourea **1a** skew on (100) with the probed (001)-face on top; dotted H-bonds are included to highlight the ribbons that are vertical under (001) and run along the *a*-axis parallel to (010); large circles are S; medium circles are N; small circles are H; C is not highlighted.

hexanedione or dimedone and dehydracetic acid **15** can be reacted in the solid-state with aniline derivatives. It is unnecessary to use acid catalysis, solvents, or liquid phases and the highly versatile enamine ketones **14b**–**g** are obtained with 100% yield at room temperature. A further benefit of avoiding iminium salt intermediates in that synthesis is the lack of workup requirements. The versatility is evident from the numerous examples that were realized. Formerly, these reactions had been performed in liquid phases with the production of much wastes. It should be noted that liquid aniline **13a** reacts in the stoichiometric melt with 1,3-cyclohexanedione (**12a**), dimedone (**12b**) and dehydracetic acid (**15**) to give the products **14a**,**b** and **16a** in 95, 100 and 90% raw yield. In the exceptional liquid-state reaction of dimedone no workup is required, except drying. Thus, the quantitative solid-state reaction of **12b** with the complex **13i** is certainly interesting but of lower value. The stoichiometric melt yield of **16a** in the reaction of de-



hydracetic acid with liquid **13a** could be increased to 100% in the solid state by using the solid 2:1-complex of **13i** (*m.p.* 92 °C) [10] at 70 °C and 1h reaction time. The hydroquinone was easily removed. The quantitative solid-state reactions of **15** with **13b**,**c** in the ball-mill to give **16b**,**c** are easier and do not require any workup.

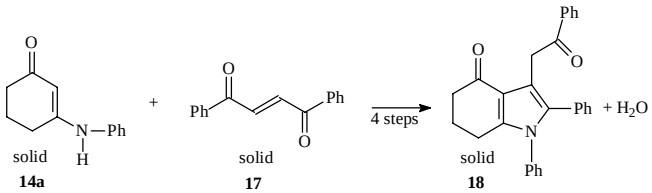
While the structures of **14** are self-evident and proven by the spectroscopic data, the structure of **16** that corresponds to those proposed by Maiti and Maitra [11] in related solution reactions requires new evidence, because further structures may be envisioned. In principle, we have to exclude the possible structures **16**' (as



proposed for related compounds by Iguchi *et al.* [12]), **16**" and **16**'". Both semiempirical PM3 or B3LYP 6-31G* density functional theory calculations (for Ar = Ph) estimate the structure **16**'" as the most stable isomer in the depicted tautomer. The most stable tautomer of compound **16**' is 9.988 or 8.167 kcal mol^{-1} higher in energy than **16**'". The structure **16**" is calculated to be 13.981 or 20.714 and the most stable tautomer of compound **16** 20.227 or 15.363 kcal mol^{-1} higher than **16**'". Thus, we have a kinetically controlled reaction that gives the same product **16a** also in ethanol solution or in the melt. **16**' and **16**" are excluded for **a**–**c** because we get loss of the acetyl group (M – 42) in the mass spectra of the compounds **16a**–**c**. Isomer **16**"**a** was independently synthesized by Pierce *et al.* [13]. It has a higher *m.p.* (142–145 °C) and different ^{1}H NMR-signals [13]. Fortunately the reaction of diketene with aniline gives a compound that has been assigned to structure **16**'"**a** (Ar = Ph) by Dehmlow *et al.* [14] and that is different from the derivative **16a** as obtained from **15**. The chemical distinction between the structures **16** and **16**"' was achieved by treatment with aqueous 2n-NaOH, followed by neutralization with 2n-HCl. Compound **16a** gives a good yield of **15**, while **16**'"**a** does not change under the same conditions. Thus, the structural assignments are correct.

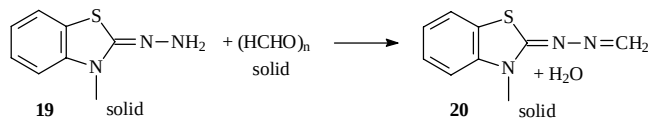
3. Cascade Reactions with Enamine Ketones

Enamine ketones such as **14a** or open chain derivatives have been used in solid-state 4-cascades that proceed with 100% yield in the solid state [15]. Thus, ball-milling of **14a** with 1,2-dibenzoylethene **17** yields **18** with 100% yield even though four distinct reaction steps (vinylogous Michael additions, imine/enamine rearrangement, cyclization, elimination) have to occur in the solid state [15]. It is remarkable that no acid catalysis is required here. Anyhow, solid-state chemistry allows for quantitative multistep cascades in a ball-mill.

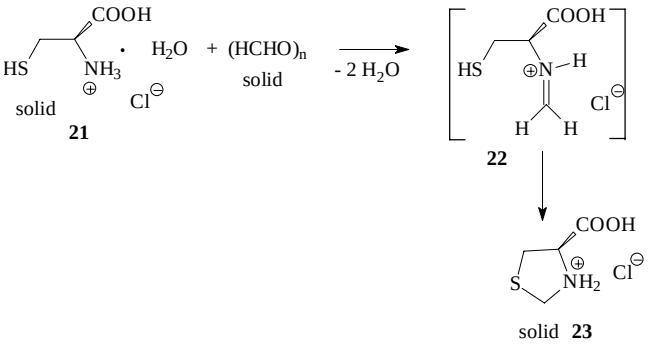


4. Methylene Imines, Internal Trapping of Methylene Iminium Salts

Paraformaldehyde can be most easily used as a source of formaldehyde when ball-milled at room temperature and methylenations occur in the presence of solid amines. While methylene imines from anilines are labile, the methylene azine **20** [16] is quantitatively obtained from the solid hydrazone **19** by this technique. The water of reaction is included by the crystal.



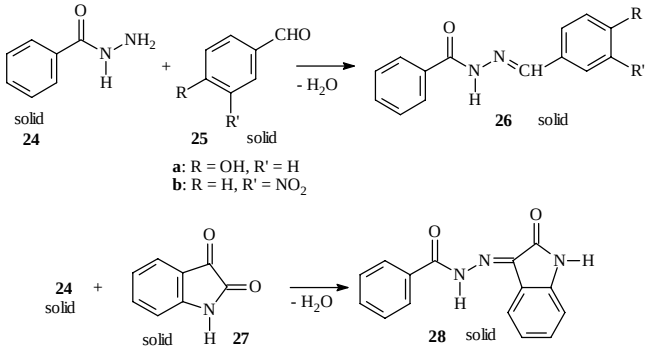
Even methylene iminium salts can be formed from ammonium salts and paraformaldehyde in the ball-mill. They are, however, extremely labile but can be efficiently trapped by adjacent thiol groups. Thus, the reaction of (*L*)-cysteine hydrochloride monohydrate **21** yields the (*L*)-thiazolidine hydrochloride **23**, presumably *via* **22**.



5. Benzoylhydrazones

Solid-solid techniques profit from increased reactivity if the three mechanistic requirements [3, 4, 5] are fulfilled. Thus, the common acid catalysis may be avoided in the quantitative synthesis of hydrazones, and if the reaction partners are used in a 1:1-ratio, no wastes are formed in the 100% yield reactions. In fact, the iminium salts are avoided in this approach.

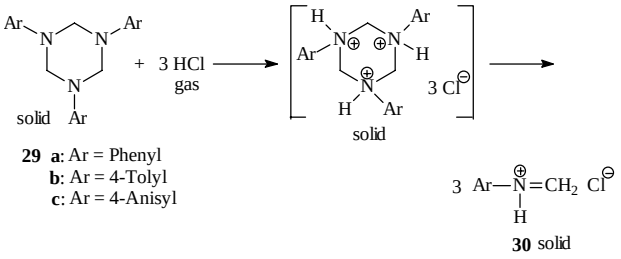
Benzhydrazide **24** and the solid aldehydes **25** are ball-milled for 1 h at 25–30 °C to give **26** in spectroscopically pure form. The *m.p.*s are the same as those found for the products from acidic solution [17].



The ketone **27** (isatine) and **24** require 3 h ball-milling for a complete reaction to give **28** and H_2O. Thus, isatine's reactivity, including all solid-state effects, is low, though a 100% yield of the same regioisomer is obtained as in solution (yield 75% in solution [18]). The structure of **28** has been secured by cyclization reactions [18].

6. Highly Sensitive Iminium Salts

Gas-solid reactions of easily available hexahydro-1,3,5-triazines **29** with HCl provide a versatile access to extremely hydrolyzable solid hydrochlorides of *N*-arylmethylene imines **30**, probably in quantitative yield. The salts **30** are only accessible in the solid state. The reactions have to be run cautiously in order to avoid rise of the temperature up to melting. Compounds **30** are characterized by their strong IR frequences at 1 733 and 1 714 cm^{-1} (C=N) [1].



The energetics in this unusually versatile synthesis of methylene imine hydrochlorides were calculated by semiempirical PM3 and DFT calculations at the level of B3LYP 6-31G* for **30a**. The presumed three-fold protonated *all-cis*-hexahydrotriazine (more favorable than *cis, trans, trans*- by 2.551 or 6.669 kcal mol^{-1}) is higher in energy content than three phenylmethylene iminium cations by 200.039 (PM3) or 204.935 kcal mol^{-1} (DFT). Even the diprotonated hexahydrotriazine is 67.232 (PM3) or 39.103 kcal mol^{-1} (DFT) above two phenylmethylene iminium ions and one phenylmethylene imine. Thus, the [2+2+2]-cycloreversion is well exothermic, notwithstanding entropic factors that were not taken into account.

The new reagents **30** are highly reactive. Despite their extreme sensitivity towards moisture, which requires the IR spectra to be taken in dried paraffine oil with unground crystals, the crystals are not deliquescent and look unchanged for hours under a microscope when left in moist air. Nevertheless, they degrade more rapidly after exposure to air. The reasons for this behavior have been elucidated with the supermicroscope AFM. Figure 3 shows a typical surface passivation on the main face of a 0.5 mm plate of **30a**. The first AFM image (7 min) of a fresh crystal in air (the relative humidity was 35%) gave craters with depths of 15 and 35 nm and a roughness of R_{ms} = 4.84 nm (Figure 3). After 60 min the craters reached their final depth of 90 nm and island hills grew up to 75 nm height (R_{ms} = 17.44 nm). The further change was very slow. At 120 min (almost identical at 160 min) the R_{ms} peaked at 20.50 nm. The surface structures became not higher after 20 h (R_{ms} = 19.95 nm). Clearly, new compounds have formed at the sur-

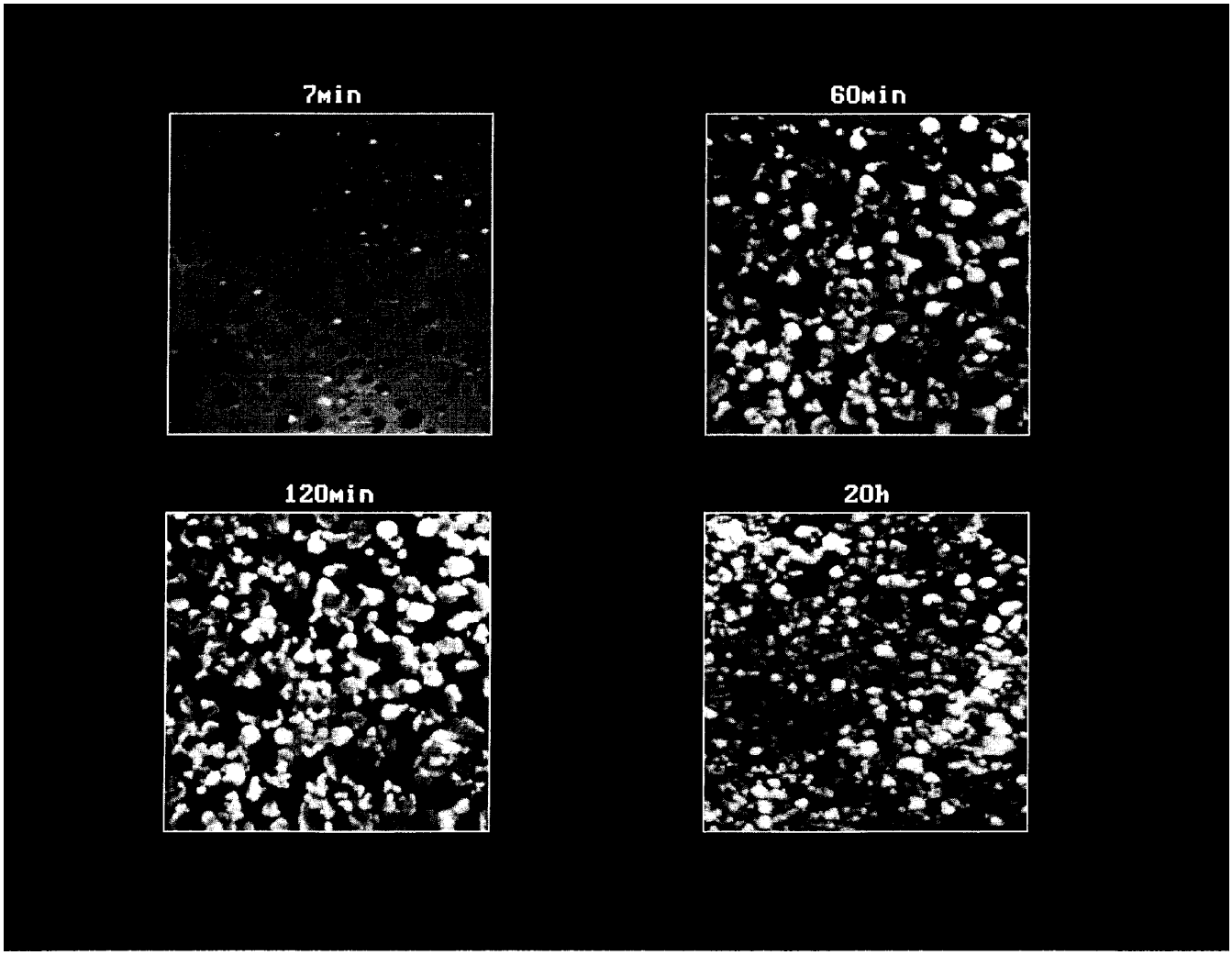
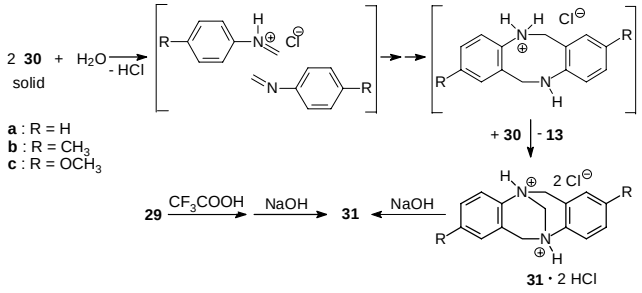


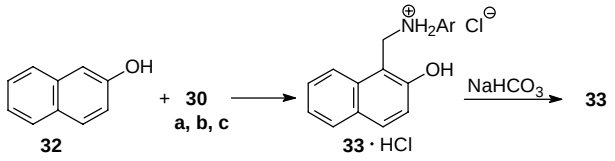
Fig. 3 5µm AFM topographies on the main surface of a 0.5 mm **30a**-crystal upon exposure to air of 35% relative humidity at 22 °C at the times indicated; the z-scales are 100 nm in the first and 200 nm in the other images.

face, but severe passivation would protect the crystal. It has to be concluded that finest grinding by a ball-mill will be essential in planned gas-solid reactions with solid **30a**.

Chemical use of the iminium salts **30** should be performed soon after their preparation, because they degrade even in a dry atmosphere, as may be judged by the decrease of the 1733 and 1713 cm^{-1} IR-absorptions (unground crystals embedded in dry paraffine oil; these bands could never be seen in a KBr pellet). Similarly, the progress of reaction of **30a**–**c** can be judged by such decrease down to the weak aromates' overtone and combination bands in that region. **30a** readily forms polymers, probably due to its free *p*-position. The new reagents **30** are useful building blocks. Weak gaseous nucleophiles such as water apparently deprotonate **30**. Thus, water vapor when applied to **30a**,**b** and **c** forms 1:1-mixtures of Troeger's bases **31a**–**c** and the respective aniline component **13a**–**c** in complex solid-state cascade reactions. These have been elucidated by spectroscopic and chemical analyses. That 3-cascade (*cf.* Section 3) requires cyclizing double arylaminomethylation and methylenation of the tetrahydro-1,5-diazocine intermediate. Deliquescence of the products **31**·2HCl starts only after complete loss of the characteristic IR bands. Clearly, the 3-cascades are catalyzed by H_2O in the solid-state. Further evidence for the solid-state 3-cascade is provided by the reactions of **30a**–**c** with "solidified" water. Thus, the crystal water of $MgSO_4 \cdot 7H_2O$ does a similar job upon cogrinding, giving a solid mixture that contains a 15, 40 and 55% yield of the Troe-ger's bases **31a**,**b**,**c**, respectively. Unfortunately, the polymerization of **30a** is also favored by that treatment. The most reasonable mechanistic interpretation is acid/base interaction that will create differences in charge density of the reacting monomers **30** and thus facilitate the arylaminomethylations. Interestingly, the Troeger's bases are also formed when the crystals of **30** are dissolved in moist $CDCl_3$. It is unclear if these reactions occur at the solid-liquid interface or in solution. A clue was found

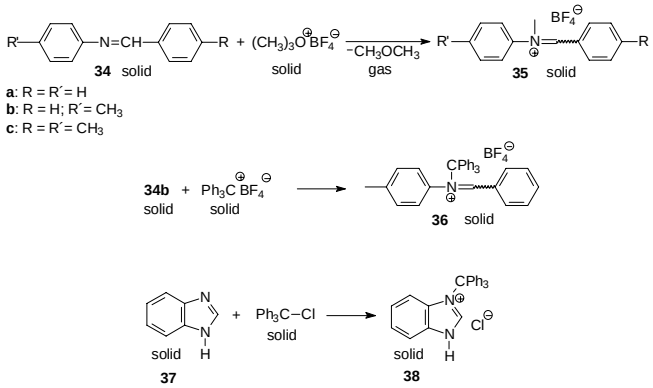


by making use of the above B3LYP DFT results which indicated that even diprotonated hexahydro-1,3,5-triazines **29** are unstable with respect to their [2+2+2]-cycloreversion products. Thus, the strong liquid trifluoroacetic acid should be able to induce formation of the methylene iminium cations **30** in solution and it was interesting to look, if the cascade reaction to give Troeger's bases **31** would work equally well in solution. It turned out, that 1:1-mixtures of **31a**,**b**,**c** and **13a**,**b**,**c** were obtained in yields of 90, 79, and 87%, respectively, just by dissolving **29a**,**b**,**c** in CF_3COOD at room temperature. It is most versatile to formulate a liquid-state 4-cascade (including the cycloreversion but not counting protonations) similar to the solid-state reaction sequence *via* the trifluoroacetates of **30a**,**b**,**c**. In view of these liquid-state results it is highly remarkable that **30a**,**b**,**c** survive in the crystalline state. Due to that favorable situation, new possibilities for mixed arylaminomethylations are opened. This was demonstrated with the solid-state reactions of β-naphthol **32** and the new reagents. Good yields of **33a**–**c** were obtained in a ball mill. The yields were less than 100% in these cases due to intermediate melting to viscous oils that could not yet be avoided. Anyhow these results look very promising for further synthetic use of **30** [19].



Another point of interest are alkylated quaternary iminium salts. They are quantitatively available from solid imines **34** with solid alkylating agents such as trimethyloxonium or triphenylcarbenium tetrafluoroborate to give **35** or **36**. The gaseous dimethylether that was formed in the synthesis of **35** escaped through a Teflon gasket that was set at 50 Nm torque. These crystalline compounds are highly deliquescent and are characterized by their C=N vibrations at 1712–1715 cm^{-1}.

Similarly, 1:1 mixtures of benzimidazole **37** and tritylchloride give the deliquescent salt **38** quantitatively in the ball mill. Some iodides, tosylates and perchlo-



rates of type **35** iminium salts have been reported in the literature [19a], but except hydrolysis no reaction or synthetic applications are known. Their now easier access should certainly stimulate the synthetic use of quaternary iminium salts.

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Experimental

FT-IR spectra were taken in KBr and in Nujol (paraffine oil that was dried with CaH_2), the latter without grinding, because ground materials of **30**, **35**, **36**, **38** degraded rapidly in air. The DMSO-D_6-content in the NMR-solvent mixtures ranged from 10 – 20%. PM3 and B3LYP (basis set 6-31G*) calculations with full geometry optimization were performed with the program TITAN, Version 1.01 of Wavefunction, Inc. Zero point vibrational energy corrections were calculated with the program Jaguar 3.5, release 42, Schrodinger, Inc., Portland, Oregon. The use of the AFM (Nanoscope II) has been described elsewhere in detail [3, 4, 5]. The images of Fig. 1 and 3 are available in color from the electronic version of this paper. The molecular migration direction in the solids was determined by tlc: a 1 cm crystal plate of **1a** (from methanol) was covered with a layer of ten 20–30 µg crystallites of **2** and a second crystal plate of **1a** was put on top. After 1 day the sandwiched crystallites were collected with a needle. tlc analysis on SiO_2 first with CH_2Cl_2 and second with CH_3OH showed the presence of product **3a**. Conversely, a crystal of **1a** was immersed in the powder of **2** and left for 2 days. All dust was removed with a paint-brush and a slight air-stream under microscopic control. No product **3a** could be detected by tlc in that crystal of **1a**.

Solid-solid-reaction of Thioureas 1 with Phenacyl bromide 2

2.00 mmol thiourea **1** or **4** and 398 mg (2.00 mmol) phenacylbromide **2** were ball-milled at room temperature for 30 min (**4**: 1 h). After drying at 0.01 bar at 80 °C quantitative yields of the pure products were obtained in all cases.

2-Amino-4-phenyl-thiazole hydrobromide (**3a**)

m.p. 184 °C; lit.: 184–186 °C [7]. – IR (KBr): ν/cm^{-1} = 3444 (N–H), 3180 (N–H), 1644 (C=N), 1603 (C=C). – ^{1}H NMR (300 MHz, D_2O): δ/ppm = 7.58 (m, 2H), 7.46 (m, 3H).

2-Methylamino-4-phenyl-thiazole hydrobromide (**3b**)

m.p. 150 °C; lit.: 149–151 °C [7]. – IR (KBr): ν/cm^{-1} = 3066 (N–H), 1649 (C=N), 1602 (C=C). – ^{1}H NMR (300 MHz, D_2O): δ/ppm = 7.57 (m, 2H), 7.49 (m, 3H), 3.01 (s, 3H).

2-(N,N-Diphenylamino)-4-phenyl-thiazole hydrobromide (**3c**)

m.p. 152–154 °C. – IR (KBr): ν/cm^{-1} = 3288 (N–H), 1600 (C=C), 1548 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 7.85 (d, 2H), 7.39 (m, 12H), 7.30 (m, 2H). – HRMS (CI, Isobutane): $C_{21}H_{17}N_2S$ $(M+H)^+$ calcd.: 329.1163 found: 329.1168.

1-Methyl-2-methylamino-4-phenyl-thiazolium bromide (**3d**)

m.p. 152 °C. – IR (KBr): ν/cm^{-1} = 3163 (N–H), 1632 (C=N). – ^{1}H NMR (300 MHz, D_2O): δ/ppm = 7.45 (m, 5H), 3.09 (s, 3H), 2.78 (s, 3H). – HRMS (CI, Isobutane): $C_{11}H_{13}N_2S$ $(M+H)^+$ calcd.: 205.0712 found: 205.0702.

1-Methyl-4-phenyl-2-phenylamino-thiazolium bromide (**3e**)

m.p. 268 °C. – IR (KBr): ν/cm^{-1} = 3156 (N–H), 2860 (N–H), 1604 (C=C), 1573 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 7.48 (m, 10H), 7.27 (m, 3H), 7.11 (m, 3H). – HRMS (CI, Isobutane): $C_{21}H_{16}N_2S$ $(M+H)^+$ calcd.: 330.1180 found: 330.1181.

2-(4-Chlorophenylamino)-1-methyl-4-phenyl-thiazolium bromide (**3f**)

m.p. 251 °C. – IR (KBr): ν/cm^{-1} = 3049 (N–H), 2784 (N–H), 1595 (C=C), 1565 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 7.53 (m, 7H), 7.13 (s, 1H), 3.79 (s, 3H). – HRMS (CI, Isobutane): $C_{16}H_{15}ClN_2S$ $(M+H)^+$ calcd.: 301.0561 found: 301.0560.

1-Methyl-2-dimethylamino-4-phenyl-thiazolium bromide (**3g**)

m.p. 150–154 °C. – IR (KBr): ν/cm^{-1} = 3408 (N–H), 3163 (N–H), 1625 (C=N). – ^{1}H NMR (300 MHz, D_2O): δ/ppm = 7.25 (m, 5H); 4.41 (s, 3H), 3.15 (s, 3H), 2.82 (s, 3H). – HRMS (CI, Isobutane): $C_{12}H_{16}N_2S$ $(M+H)^+$ calcd.: 220.1346 found: 220.1381.

[4H,5H]-2-Phenacylthio-imidazoline hydrobromide (**5**) and *3-Phenyl-5,6-dihydro[7H]<2,1-b>thiazolium bromide* (**6**)

204 mg (2.00 mmol) 2-imidazolidine thione **4** and 398 mg (2.00 mmol) phenacylbromide **2** were ball-milled at room temperature for 30 min. After drying at 0.01 bar at 80 °C 600 mg (100%) **5** were obtained. *m.p.* 251 °C, lit.: 251–253 °C [7b]. – IR (KBr): ν/cm^{-1} = 3109 (N–H), 2899 (N–H), 1684 (C=O). 301 mg (2.00 mmol) **5** were heated to 165 °C for 60 min. After evacuation 280 mg (100%) of the hydrobromide **6** were obtained. *m.p.* 251 °C, lit.: 251–253 °C [20]. – IR (KBr): ν/cm^{-1} = 2989 (N–H), 2883 (N–H), 1582 (C=N). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 7.55 (m, 5H), 6.83 (s, 1H), 4.60 (t, 2H), 4.49 (t, 2H).

2-Phenacylthiobenzimidazole hydrobromide (**8**)

300 mg (2.00 mmol) 2-mercaptobenzimidazole (**7**) and 398 mg (2.00 mmol) phenacylbromide **2** were ball-milled at room temperature for 1 h. After drying at 0.01 bar at 80 °C 697 mg (100%) **8** were obtained. *m.p.* 233, lit.: 233–234 °C [21]. – IR (KBr): ν/cm^{-1} = 2921 (N–H), 2845 (N–H), 2765 (N–H), 1677 (C=O). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 8.12 (d, 2H), 7.71 (m, 3H), 7.59 (m, 2H), 7.50 (m, 2H), 5.54 (s, 2H).

2-Acetonylthiobenzimidazole hydrobromide (**11**)

334 mg (2.00 mmol) mercaptobenzothiazole (**9**) were evacuated in a 100 mL flask and connected to a vacuum line with a 100 mL flask that contained 500 mg (5.4 mmol) chloroacetone **10** and the whole setup left for 12 h at 60 °C. Excess **10** and the water of reaction were removed by evaporation. 520 mg (100%) **11** were obtained. *m.p.* 168 °C. The *m.p.* of the free base, after treatment with K_2CO_3-solution, was 65 °C, lit.: 65–67 °C [22]. – IR (KBr): ν/cm^{-1} = 1717 (C=O). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 7.69 (d, 1H), 7.50 (d, 1H), 7.24 (t, 1H), 7.12 (t, 1H), 4.16 (s, 2H), 2.19 (s, 3H).

Enamine Ketones 14

Melt reactions: 2.00 mmol of the 1,3-dicarbonyl compound **12a**,**b** or **15** and 186 mg (2.00 mmol) aniline (**13a**) were placed in a 50 mL flask, evacuated and heated to 80 °C for 1 h in a drying oven. The solid product was dried at 0.01 bar at 80 °C and the yield determined by weight and ^{1}H NMR estimate. 85, 100 and 90% **14a**, **14b** and **16a** were formed.

Solid-state reactions: 2.00 mmol 1,3-dicarbonyl compound **12** and 2.00 mmol of the solid aniline derivative **13** were ball-milled at room temperature for 30 min. After drying at 0.01 bar at 80 °C pure enamine ketone **14** was obtained with quantitative yield.

3-Phenyl-cyclohex-2-ene-1-one (**14a**)

14a had been previously isolated from a stoichiometric melt in 65% or 70% yield [23]. If the stoichiometric melt reaction was run as described above, 95% of **14a** ensued with 5% of unreacted aniline and a not elucidated side-product.

5,5-Dimethyl-3-phenyl-cyclohex-2-ene-1-one (**14b**)

280 mg (2.00 mmol) dimedone **12b** and 296 mg (1.00 mmol) hydroquinone-aniline 1:2 complex **13i** (synthesized by recrystallization of hydroquinone from aniline in 83% yield) were ball-milled at 70 °C for 1 h. The hydroquinone was removed by 5 min trituration with 20 ml of water, filtration, and three washings with 2 mL of water each and the residue was dried at 0.01 bar. The yield was 430 mg (100%) of pure **14b**. *m.p.* 179 °C, lit.: 179–180 °C [24]. – IR (KBr): ν/cm^{-1} = 3237 (N–H), 1597 (C=C), 1573 (C=O). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.23 (m, 2H), 7.12 (m, 3H), 5.52 (s, 1H), 2.37 (s, 2H), 2.20 (s, 2H), 1.09 (s, 6H).

3-p-Toluidino-cyclohex-2-ene-1-one (**14c**)

m.p. 139 °C, lit.: 140–141°C [24]. – IR (KBr): ν/cm^{-1} = 3253 (N–H), 1609 (C=C), 1575 (C=O), 1538 (C=C), 1511 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.12 (s, 1H), 7.09 (AA'BB', 2H), 7.00 (BB'AA', 2H), 5.45 (s, 1H), 2.48 (t, 2H), 2.34 (m, 2H + 3H), 1.96 (m, 2H).

3-p-Anisidino-cyclohex-2-ene-1-one (**14d**)

m.p. 158 °C, lit.: 160–161 °C [24]. – IR (KBr): ν/cm^{-1} = 3217 (N–H), 1609 (C=C), 1571 (C=O), 1537 (C=C), 1511 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.07 (s, 1H), 7.03 (AA'BB', 2H), 6.82 (BB'AA', 2H), 5.32 (s, 1H), 3.78 (s, 3H), 2.48 (t, 2H), 2.30 (t, 3H), 1.99 (m, 2 H).

3-p-Chloranilino-cyclohex-2-ene-1-one (**14e**)

m.p. 189 °C, lit.: 190 °C [25]. – IR (KBr): ν/cm^{-1} = 3250 (N–H), 1603 (C=C), 1570 (C=O), 1520 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.36 (br.p, 1NH), 7.24 (AA'BB', 2H), 7.08 (BB'AA', 2H), 5.45 (s, 1H), 2.50 (t, 2H), 2.33 (m, 2H), 1.92 (t, 2H).

5,5-Dimethyl-3-p-toluidino-cyclohex-2-ene-1-one (**14f**)

m.p. 194 °C, lit.: 196–197 °C [24]. – IR (KBr): ν/cm^{-1} = 3244 (N–H), 3187 (N–H), 1609 (C=C), 1576 (C=O), 1527 (C=C), 1515 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.20 (AA'BB', 2H), 7.02 (BB'AA', 2H), 5.49 (s, 1H), 2.30 (br.p, 2H + 3H), 2.19 (s, 2H), 1.08 (s, 6 H).

5,5-Dimethyl-3-p-anisidino-cyclohex-2-ene-1-one (**14g**)

m.p. 225 °C, lit.: 227–230 °C [26]. – IR (KBr): ν/cm^{-1} = 3207 (N–H), 1608 (C=C), 1569 (C=O), 1535 (C=C), 1510 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.10 (d, 2H), 6.89 (d, 2H), 5.38 (s, 1H), 3.81 (s, 3H), 2.32 (s, 2H), 2.21 (s, 2H), 1.10 (s, 6 H).

6,6-Dimethyl-3-p-chloranilino-cyclohex-2-ene-1-one (**14h**) [27]

m.p. 199 °C. – IR (KBr): ν/cm^{-1} = 3247 (N–H), 1602 (C=C), 1577 (C=O), 1537 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.23 (AA'BB', 2H), 7.11 (br. p, 1NH), 7.06 (BB'AA', 2H), 5.39 (s, 1H), 2.50 (t, 2H), 1.81 (t, 2H), 1.11 (s, 6H).

3-Acetyl-2-anilino-6-methyl-4-pyrone (**16a**)

336 mg (2.00 mmol) dehydracetic acid **15** and 296 mg (1.00 mmol) hydroquinone-aniline 1:2 complex **13i** were ball-milled at 70 °C for 1 h. The hydroquinone was removed by 5 min trituration with 20 mL water, filtration, and three washings with 2 mL of water each and the residue was dried at 0.01 bar. The yield was 481 mg (99%). *m.p.* 128 °C; the same product can be obtained in boiling ethanol solution, though in lower yield. – IR (KBr): ν/cm^{-1} = 1697 (C=O), 1660 (C=O), 1558 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 15.61 (br.p, 1H), 7.41 (m, 3H), 7.18 (m, 2H), 5.79 (s, 1H), 2.61 (s, 3H), 2.20 (s, 3H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 184.88, 175.33, 163.77, 163.37, 136.35, 129.60 (2C), 128.13, 125.59 (2C), 107.27, 97.31, 20.28, 19.87; structure **16'a** had been formerly assigned to this compound [14].
Conversion to **15**: 243 mg (1.00 mmol) **16a** and 23 mg (1.00 mmol) NaOH were dissolved in 20 mL water and heated to boiling for 2 h. After cooling it was acidified with 2n-HCl. An 80% yield of dehydracetic acid was collected; *m.p.* and IR were identical with those of an authentic sample; *m.p.* 113 °C. – IR (KBr): ν/cm^{-1} = 1718, 1637 (C=O).

3-Acetyl-2-[4-toluidino]-6-methyl-4-pyrone (**16b**)

336 mg (2.00 mmol) dehydracetic acid **15** and 214 mg (2.00 mmol) 4-toluidine (**13c**) were ball-milled at room temperature for 1 h. After drying at 0.01 bar at 80 °C 514 mg (100%) **16b** were obtained, *m.p.* 155–156 °C; the same product can be obtained in boiling ethanol solution, though in lower yield. – IR (KBr): ν/cm^{-1} = 1699 (C=O), 1661 (C=O), 1568 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.21 (AA'BB', 2H), 7.05 (BB'AA', 2H), 5.75 (s, 1H), 2.62 (s, 3H), 2.41 (s, 3H), 2.13 (s, 3 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 185.09, 175.76, 163.92, 163.51, 138.58, 134.15, 130.56 (2C), 125.76 (2C), 107.79, 97.71, 28.09, 20.63, 20.26. – MS (EI): *m/z* (%) = 257 (M^+, 100), 256 (86), 242 (18), 214 (16), 172 (20), 132 (32). – HRMS (EI): $C_{15}H_{15}NO_3$ calcd.: 257.1052 found: 257.1052.

3-Acetyl-2-[4-anisidino]-6-methyl-4-pyrone (**16c**)

336 mg (2.00 mmol) dehydracetic acid **15** and 246 mg (2.00 mmol) 4-anisidine (**13d**) were ball-milled at room temperature for 1 h. After drying at 0.01 bar at 80 °C 545 mg (100%) enamine **16c** were obtained. *m.p.* 175–177 °C; the same product can be obtained in boiling ethanol solution, though in lower yield. – IR (KBr): ν/cm^{-1} = 1696 (C=O), 1659 (C=O), 1560 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.21 (AA'BB', 2H), 6.94 (BB'AA', 2H), 5.73 (s, 1H), 3.80 (s, 3H), 2.60 (s, 3H), 2.18 (s, 3H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 185.06, 175.87, 164.02, 163.48, 159.59, 129.46, 127.12 (2C), 115.16 (2C), 107.76, 97.63, 55.93, 20.56, 20.24. – MS (EI): *m/z* (%) = 273 (M^+, 100), 258 (16), 217 (8), 188 (10), 174 (18). – HRMS (EI): $C_{15}H_{15}NO_4$ calcd.: 273.1007 found: 273.1006

3-Acetyl-4-hydroxy-6-methyl-1-phenyl-pyridone-2 (**16'''a**) [14]

Compound **16'''a** was synthesized according to the literature procedure. *m.p.* 220 °C, lit.: 219–220 °C. – IR (KBr): ν/cm^{-1} = 1658 (C=O), 1619 (C=O). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 15.76 (s, 1H), 7.56 (m, 3H), 7.20 (m, 2H), 5.91 (s, 1H), 2.68 (s, 3H), 1.99 (s, 3H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 205.77, 176.24, 163.42, 153.75, 138.02, 129.86 (2C), 129.01, 128.10 (2C), 105.79, 100.88, 31.21, 22.20.
Treatment with base: 243 mg **16a** (1.00 mmol) and 23 mg (1.00 mmol) NaOH were dissolved in 20 mL water and heated to boiling for 2 h. After cooling and acidification with 2n HCl unchanged **16a** separated in over 80% yield. The *m.p.* and IR were identical with the starting compound.

Formaldehyde-(3-methyl-benzothiazolone-2)-hydrazone (**20**) [16]

358 mg (2.00 mmol) 3-methyl-benzothiazolone-2-hydrazone (**19**) and 60 mg (2.00 mmol) paraformaldehyde were ball-milled at room temperature for 1 h. After drying at 0.01 bar at 60 °C 381 mg (100%) **20** were obtained. *m.p.* 85 °C. – IR (KBr): ν/cm^{-1} = 1621, 1568. – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.41 (m, 2H), 7.29 (t, 1H), 7.06 (m, 2H), 6.72 (d, 1H), 3.51 (s, 3H).

(R)-Thiazolidine-4-carboxylic acid hydrochloride (**23**)

351 mg (2.00 mmol) (*L*)-cysteine hydrochloride monohydrate (**21**) and 60 mg (2.00 mmol) paraformaldehyde were ball-milled at room temperature for 1 h. After drying at 0.01 bar at 80 °C 338 mg (100%) of **23** were obtained. *m.p.* 184 °C, lit.: 184–185 °C [28]. – IR (KBr): ν/cm^{-1} = 2870 (N–H), 2716

(N–H), 2 558 (N–H), 1 735 (C=O). – ^{1}H NMR (300 MHz, D_2O): δ/ppm = 4.63 (t, 1H), 4.31 (m, 2H), 3.38 (m, 2H).

Benzoylhydrazones 26 and 28

272 mg (2.00 mmol) benzhydrazide **24** and 2.00 mmol of the carbonyl compounds **25** or **27** were ball-milled at room temperature for 1 h or 3 h, respectively. After drying at 0.01 bar at 80 °C **26** and **28** were obtained in quantitative yields.

N-(4-Hydroxyphenyl)-benzoylhydrazone (**26a**)

m.p. 229 °C, lit.: 233 °C [17]. – IR (KBr): ν/cm^{-1} = 3 406 (O–H), 3 206 (N–H), 1 632 (C=O), 1 608 (C=N; C=C). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 8.25 (s, 1H), 7.9–7.8 (m, 2H), 7.51 (AA'BB', 2H), 7.4–7.25 (m, 3H), 6.75 (BB'AA', 2H).

N-(3-Nitrophenyl)-benzoylhydrazone (**26b**)

m.p. 190 °C, lit.: 192 °C [17]. – IR (KBr): ν/cm^{-1} = 3 223 (N–H), 1 646 (C=O), 1 605 (C=N; C=C), 1 527 (NO_2), 1 354 (NO_2). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 8.59 (s, 1H), 8.21 (m, 2H), 7.86 (m, 2H), 7.66–7.43 (m, 5H).

Isatine-3-benzoylhydrazone (**28**)

m.p. 289 °C, lit.: 267 °C [18]. – IR (KBr): ν/cm^{-1} = 3 195 (N–H), 1 697 (C=O), 1 678 (C=O), 1 624 (C=N; C=C). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 14.1 (br.p, 1NH), 10.49 (br.p, 1NH), 7.95 (br.s, 2H), 7.79 (br. s, 1H), 7.58 (m, 3H), 7.29 (br.s, 1H), 7.10 (m, 1H), 6.97 (m, 1H).

Methylene Iminium Salts

Anilinomethylene hydrochloride (**30a**)

1.00g (3.17 mmol) of crystalline 1,3,5-triphenylhexahydrotriazine (**29a**) were cooled to –18 °C in an evacuated 500 mL flask and 500 mL HCl gas (1 bar) were let in through a vacuum line in 6 portions during 2 h. Excess gas was evaporated after thawing to 4 °C (8 h). A yellow solid was obtained: 1.35 g (100%). – IR (Nujol): ν/cm^{-1} = 1 733, 1 714 (C=N). – IR (KBr, decomposition products): ν/cm^{-1} = 1 662 (C=N); 1 589, 1 495 (C=C); 759, 692 (monosubst.); solutions of **30a** in not highly dried $CDCl_3$ contain no **30a**, but mostly Troeger's base **31a**, as detected by ^{1}H-NMR.

4-Toluidinomethylene hydrochloride (**30b**)

1.17 g (3.28 mmol) of crystalline 1,3,5-tris-(4-tolyl)-hexahydrotriazine (**29b**) were cooled to –10 °C in an evacuated 500 mL flask and 500 mL HCl gas (1 bar) were continuously let in through a stopcock in 3 h. Excess gas was evaporated and an orange solid was obtained after 8 h at 4 °C: 1.53 g (100%). – IR (Nujol): ν/cm^{-1} = 1 733, 1 714 (C=N). – IR (KBr, dec. prod.): ν/cm^{-1} = 1 627 (C=N); 1 592, 1 510 (C=C); 811 (1,4-disubst.); solutions of **30b** in not highly dried $CDCl_3$ contain no **30b**, but mostly Troeger's base **31b**, as detected by ^{1}H NMR.

4-Anisidinomethylene hydrochloride (**30c**)

1.00 g (2.47 mmol) of crystalline 1,3,5-tris-(4-anisyl)-hexahydrotriazine (**29c**) were cooled to –10 °C in an evacuated 1 L flask and 500 mL HCl gas were continuously let in through a stopcock in 3 h. Excess gas was evaporated and a brown solid was obtained after 8 h at 4 °C: 1.27 g (100%). – IR (Nujol): ν/cm^{-1} = 1 733, 1 714 (C=N). – IR (KBr, dec. prod.): ν/cm^{-1} = 1 662 (C=N); 1 613, 1 511 (C=C); 827 (1,4-disubst.); solutions of **30c** in not highly dried $CDCl_3$ contain no **30c**, but mostly Troeger's base **31c**, as detected by ^{1}H NMR.

Troeger's Bases

Gas-solid: ca. 2 mmol of the methylene iminium chlorides **30a**,**b**,**c** were ball-milled for 5 min and then spread on a watch glas with 15 cm diameter in air of 35% relative humidity at 22 °C. The characteristic C=N IR-bands had disappeared after 1 h and the material became deliquescent. ^{1}H NMR spectra showed the characteristic peaks of the corresponding Troeger's bases **31a**,**b**,**c** (peak positions after washing with NaHCO_3 solution) and the yields were determined by integration. Soild-solid: 1.0 g **30a**,**b**,**c** and 10 g $MgSO_4 \cdot 7H_2O$ were co-ground in a mortar for 10 min. The solid crystalline mixture was five times extracted with 30 mL methylene chloride each by using a centrifuge, and the yields were determined by integration. In the reaction of **30a** an obviously polymer solid remained (67%) after addition of 200 mL water, neutralization with NaOH to pH 7–8 and filtration.
Liquid-state: 30–50 mg of the hexahydrotriazines **29a**,**b**,**c** were dissolved in CF_3COOD and the yields of **31a**,**b**,**c** and of **13a**,**b**,**c** were determined by ^{1}H NMR integration. Minor side products were present. Gram-scale runs in CF_3COOH proceed exothermic and give rise to increased amounts of as yet unexplored side-products. The stoichiometric 1:1-mixtures of **13a**,**b**,**c** and **31a**,**b**,**c** and side products can be separated by chromatography after distillative removal of the solvent.

Troeger's Base (**31a**) *(R=H)* [29]

Yield solid-solid 15%; gas-solid 60%; liquid-state 90%. – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.6–7.2 (m, 8H), 5.02 (AB, J = 15 Hz, 2H), 4.71 (s, 2H), 4.34 (BA, J = 15 Hz, 2H); (300 MHz, CF_3COOD): δ/ppm = 7.6–7.35 (m, 6H), 7.26–7.18 (m, 2H), 5.25 (s, 2H), 5.21 (AB, J = 15Hz, 2H), 4.64 (BA, J = 16Hz, 2H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 139.88, 130.59, 130.09, 127.44, 124.63, 123.66, 66.68, 57.20. – ^{13}C NMR (75 MHz, CF_3COOD): δ/ppm = 139.80, 132.75, 132.35, 131.96, 129.94, 125.67, 69.80, 59.76.

Troeger's Base (**31b**) *(R = CH_3)* [30]

Yield solid-solid 40%; gas-solid 78%; liquid-state 79%. – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.05–6.9 (br. AB, 4H), 6.70 (br. s, 2H), 4.67 (AB, J = 15 Hz, 2H), 4.30 (s, 2H), 4.11 (BA, J = 15 Hz, 2H), 2.23 (s, 6H). – ^{1}H-NMR (300 MHz, CF_3COOD): δ/ppm = 7.40–7.22 (br. AB, 4H), 6.97 (br. s, 2H), 5.22 (s, 2H), 5.14 (AB, J = 15Hz, 2H), 4.53 (BA, J = 15Hz, 2H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 145.30, 133.48, 128.13, 127.44, 127.27, 124.77, 67.06, 58.66, 20.80. – ^{13}C-NMR (75 MHz, CF_3COOD): δ/ppm = 143.99, 136.21, 133.16, 130.27, 122.70, 122.47, 69.30, 59.93, 21.56.

Troeger's Base (**31c**) *(R = OCH_3)* [31]

Yield solid-solid 55%; gas-solid ca. 30%; liquid-state 87%. – ^{1}H NMR (300 MHz, CF_3COOD): δ/ppm = 7.57 (br. AB, 2H), 7.03 (br. BA, 2H), 6.66 (br. s, 2H), 5.09 (s, 2H), 5.04 (AB, J = 15 Hz, 2H), 4.45 (BA, J = 15 Hz, 2H), 3.87 (s, 6H). – ^{13}C NMR (75 MHz, CF_3COOD): δ/ppm = 158.01, 127.42, 126.44, 125.03, 119.04, 118.51, 70.32, 60.11, 57.84.

Arylaminomethylations of β-Naphthol

ca. 2 mmol of the arylmethylene imine hydrochloride **30** were sampled under dry Ar, precisely weighed and ball-milled together with the equivalent of β-naphthol **32** for 1 h. The sticky material solidified on standing. It was dissolved in CH_2Cl_2, washed with aqueous $NaHCO_3$ and the raw yield determined by ^{1}H-NMR. The pure compounds were obtained by recrystallization from ethanol.

1-Phenylaminomethyl-2-Naphthol (**33a**) [32]

Yield 50%. *m.p.* 116 °C; lit: 118–120 °C. – IR(KBr): ν/cm^{-1} = 3258 (sharp, OH); 1511 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 7.7–7.1 (m, 11H), 4.77 (s, 2H). – ^{13}C NMR (75 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 151.61, 133.26, 128.46, 127.84(2C), 127.94(2C), 125.43(2C), 123.07 (2C), 121.88(2C), 118.03, 117.73(2C), 39.32.

1-(4-Methylphenyl)-aminomethyl-2-naphthol (**33b**) [32]

Yield 65%. *m.p.* 138 °C; lit: 140–141 °C. – IR(KBr): ν/cm^{-1} = 3258 (sharp, OH); 1511 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.75–6.9 (m, 10H), 4.80 (s, 2H), 2.21 (s, 3H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 155.19, 139.41, 134.68, 132.48, 130.72, 130.34(2C), 129.92, 129.51, 123.21, 121.33, 119.22(2C), 118.27, 118.15, 110.79, 46.11, 20.64.

1-(4-Methoxyphenyl)-aminomethyl-2-naphthol (**33c**) [33]

Yield 45%. *m.p.* 131 °C; lit. 132 °C. – IR (KBr): n/cm^{-1} = 3260 (sharp, OH); 1510 (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 7.8–6.8 (m, 10H), 4.84 (s, 2H), 3.77 (s, 3H). – ^{13}C NMR (75 MHz, $CDCl_3$/DMSO-D_6): δ/ppm = 158.11, 132.53, 130.51, 127.95, 126.40, 124.11, 123.66, 122.79(2C), 122.39, 121.42, 114.71, 114.10(2C), 113.89, 109.35, 54.90, 46.22.

Alkylation of 34

ca. 2.00 mmol of non-sticky trimethyloxonium tetrafluoroborate (Aldrich) were sampled in an atmosphere of dry Ar, precisely weighed and transferred to the ball-mill together with the precise equivalent of **34c**,**d**,**e** under Ar. The Teflon gasket was closed with a torque of 50 Nm and ball-milling started for 1 h at room temperature. Dimethylether escaped during reaction and upon opening of the mill. The deliquescent solid material was collected under dry Ar. The yields were quantitative. Analysis was done by IR and NMR in $CDCl_3$.

N-Methyl-N-benzylidene-anilinium tetrafluoroborate (**35a**): IR (Nujol): ν/cm^{-1} = 1712 (C=N). – IR (KBr, dec. prod.): ν/cm^{-1} = 1634 (C=N); 1600, 1589, 1495 (C=C), 1056 ($BF4^-$), 768, 688 (monosubst.). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 3.63 (s, 3H), 7.4–7.7 (m, 10H), 9.31 (s, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 56.74, 120.91(2C), 128.62(2C), 130.17(2C), 130.95, 132.42(2C), 134.10, 136.49, 137.07, 165.43.

N-Methyl-N-benzylidene-4-toluidinium terafluoroborate **(35b)**: IR (Nujol): ν/cm^{-1} = 1732, 1713 (C=N). – IR (KBr, dec. prod.): ν/cm^{-1} = 1655 (C=N), 1605, 1497 (C=C), 1057 ($BF4^-$), 848 (1,2-disubst.), 808, 758 (monosubst.). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 2.34 (s, 3H), 4.13 (s, 3H), 7.05–7.20 (AA'BB', 4H), 7.4–7.6 (m, 5H), 9.11 (s, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 22.13, 53.76, 123.71(2C), 130.38 (2C), 131.45(3C), 134.80(2C), 136.33, 140.86, 149.85, 172.58.

N-Methyl-N-(4-methyl-benzylidene)-4-toluidinium tetrafluoroborate (**35c**): IR (Nujol): ν/cm^{-1} = 1715 (C=N). – IR (KBr, dec. prod.): ν/cm^{-1} = 1649 (C=N); 1605, 1516 (C=C); 1054 ($BF4^-$); 821 (1,2-disubst.). – ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 2.34 (s, 3H), 2.45 (s, 3H), 4.12 (s, 3H), 7.08–7.26 (AA'BB', 4H), 7.30–7.45 (AA'BB', 4H), 9.11 (s, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm = 21.30, 22.09, 53.78, 123.40(2C), 130.27 (2C), 130.87, 131.84(2C), 134.71(2C), 138.35, 141.95, 149.51, 172.42.

Reaction of Methylbenzylidene-aniline 34b with Triphenylcarbenium-tetrafluoroborate: Synthesis of *N*-Triphenylmethyl-*N*-benzylidene-4-toluidinium tetrafluoroborate (36)

195 mg (1.00 mmol) imine **34b** and 330 mg (1.00 mmol) triphenylcarbenium-tetrafluoroborate were placed in a ball-mill under argon in a glove box and milled for 1 h at room temperature. 525 mg **36** were obtained. *m.p.* 138–140 °C. – IR (Nujol): ν/cm^{-1} = 1732, 1713 (C=N). – IR (KBr, dec. prod.): ν/cm^{-1} = 1655 (C=N), 1607 (C=C), 1588 (C=C), 1491 (C=C). – HRMS (CI, Isobutane): $C_{33}H_{29}N$ $(M+H)^+$ calcd.: 439.2579 found: 439.2609.

Reaction of Benzimidazole 37 with Triphenylchloromethane: Synthesis of 1-Triphenylmethyl-3*H*-benzimidazolium chloride (38)

118 mg (1.00 mmol) benzimidazole **37** and 279 mg (1.00 mmol) triphenylchloromethane were placed in a ball-mill under argon and milled for 1 h at room temperature. 397 mg **38** were obtained. *m.p.* >149 °C (decomp.). – IR (Nujol): ν/cm^{-1} = 1730, 1713 (C=N).

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