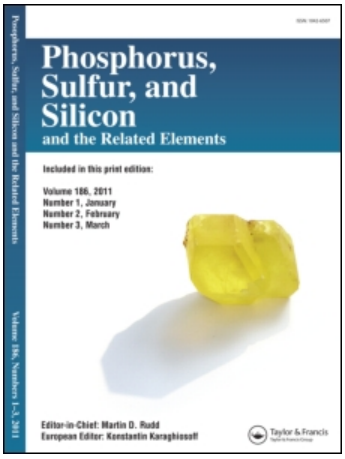


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# GAS/SOLID-REACTIONS WITH SULFUR COMPOUNDS

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# GAS/SOLID-REACTIONS WITH SULFUR COMPOUNDS

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The various types of gas/solid-reactions (addition, elimination, substitution, condensation, catalyzed cycloaddition) in different branches of sulfur chemistry (heterocycles, *S*-vinyl-compounds, thioethers, thiols, sulfur dioxide) are reviewed, new types and new synthetic applications added. The reactions run to completion in a short time. The advantages of avoiding solvents are discussed, some mechanistic hints obtained.

*Key words:* Gas/solid-reactions; salt formation; addition reactions; *S*-vinyl compounds; thiols; sulfurdioxide.



## INTRODUCTION

Organic gas/solid-reactions are barely developed and are still not well recognized even though they are highly versatile and make considerate use of the available resources by avoiding solvents.[1] In sulfur chemistry there are numerous applications in different fields which profit from the still unusual technique of reacting gases with crystals in order to generate product crystals without passing through a liquid phase. The fields are presently subdivided in the following way:

(a) Salt formation of *S*/*N*-heterocycles without affecting the sulfur function.

(b) Addition reactions to sulfur-containing compounds without affecting the sulfur function.

(c) Addition reactions to *S*-vinyl compounds.

(d) Reactions of volatile thiols.

(e) Reactions of sulfur dioxide.

We present here first examples for all of these types which proceed virtually to completion in short times and which are of preparative use.

## RESULTS AND DISCUSSION

(a) The benzothiazoles **1** are weak bases. In order to generate their solid hydrochlorides or hydrobromides gas/solid techniques are most easy and largely preferable, because there are no hydrolysis problems and the salts are more

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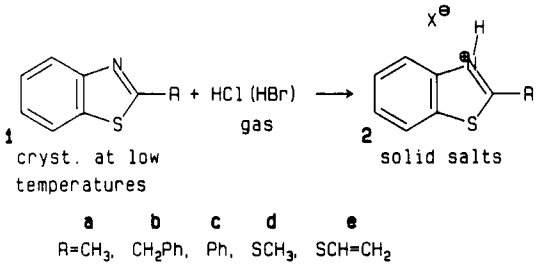
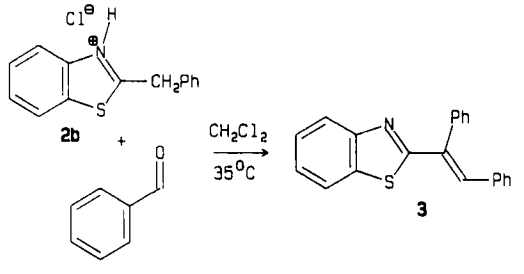
stable, if no solvent had to be removed from them. Solid bases (**1c**) are reacted at room temperature, liquid or low melting ones after cooling them down below their melting points. After evacuation excess gas (1 bar) from regular steel-cylinders is applied. The new solids form quite rapidly and quantitatively (see Table I). They are uniformely crystalline and may be handled in air (no fuming) after evaporation of the excess gas.




SCHEME 1

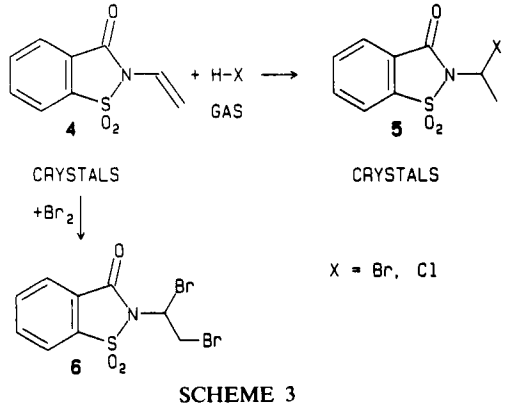
Interestingly, the *S*-vinyl compound **1e** forms only the salts with HCl and HBr, but does not add these gases to the double bond.

The salts **2** may be used as easy to handle acid catalysts. **2b** may be directly condensed with benzaldehyde to give **3**[2] and $HCl \cdot H_2O$ easily. No precautions were taken in order to remove the water which is formed during the reaction.




SCHEME 2

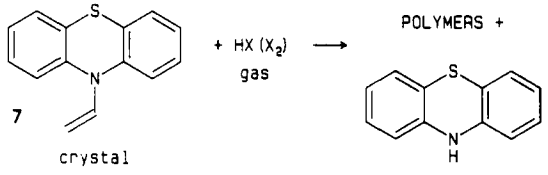
(b) Reactions of sulfur compounds with gases (HBr, HCl, HI, $Br_2$) in which the sulfur function is retained are the additions to the double bond of crystalline *N*-vinylsaccharine which have been reported recently.[1]




SCHEME 3

It is very profitable, that acid catalyzed polymerization of **4** is suppressed and that preparative runs (gram scale) are complete in about two days at room temperature. The products **5** and **6** are highly reactive $\alpha$-halogeno compounds, which may be used for various transformations, e.g. substitutions of the halogen.

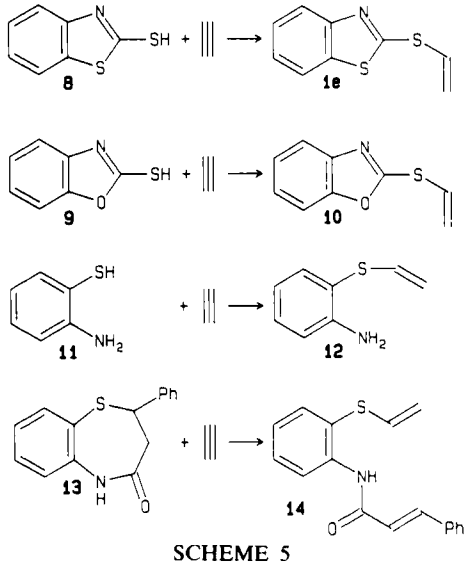
Even in gas/solid-reactions there may be the risk of polymerization. Thus, we did not succeed in obtaining 1:1-adducts, when *N*-vinylphenothiazine **7** was exposed to HCl, HBr (30 min) or $Cl_2$ (5 h) at room temperature. Dark crystals were obtained which gave broad unstructured absorptions in the $^1$H-NMR and which are therefore termed as polymers even though after chromatography some phenothiazine is isolated, apparently via hydrolysis. The nature of the polymers remains to be elucidated.




SCHEME 4

In these examples the sulfur function is off the reaction centers and remains unaffected even though there is conjugation.

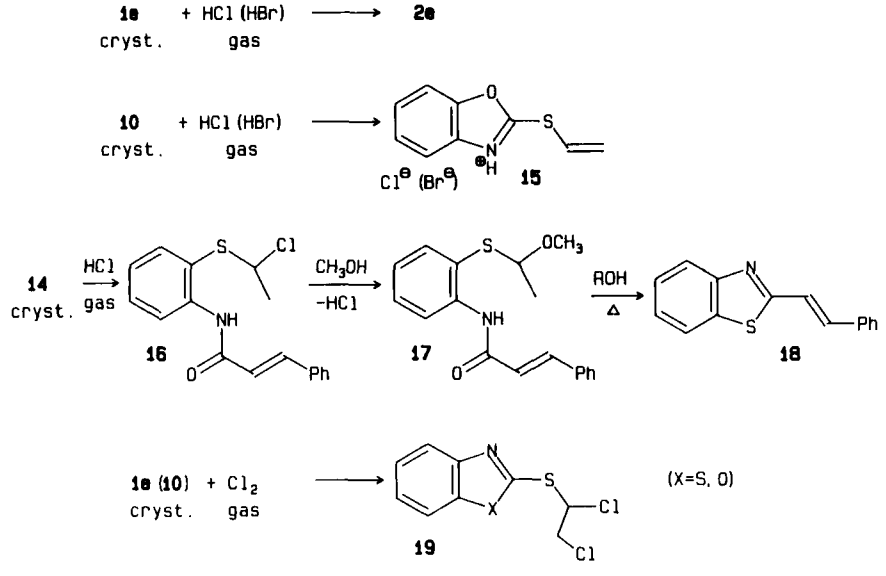
(c) *S*-vinyl-compounds are easily obtained via Reppe-vinylation.[3] Thus, **1e**, **10**, **12**, and **14** have been prepared (see Table II). It is remarkable, that the heterocycle **13** does not lead to a *N*-vinyl compound. Rather the ring-opened non-heterocyclic *S*-vinyl compound **14** is isolated after chromatographic separation from elusive side-products. These new compounds in crystalline form were exposed to the gases HCl, HBr and $Cl_2$. **1e** (see above) and **10** do not add HCl or HBr to the double bond at temperatures where they are crystalline (see Table I). Rather they form the stable salts **2e** and **15**.




SCHEME 5

Thus, once the crystalline salts are formed, they are no longer accessible to gas/solid-addition of HCl or HBr at the *S*-vinyl group. The salts are relatively high melting, e.g. 145–146°C for **2e** (hydrobromide) and 126–128°C for **15** (hydrobromide). **12** did not crystallize down to −100°C. Therefore no gas/solid-reactions could be studied.

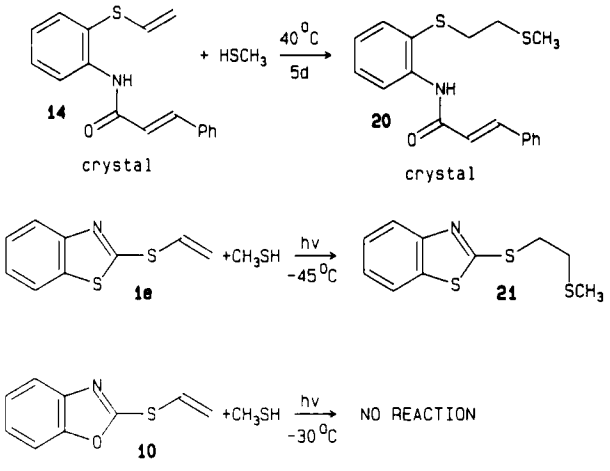
In the absence of a basic group as in **14** there is addition of HCl to the *S*-vinyl double bond of the crystalline material to give the labile **16** which is transformed into the derivative **17** in methanol. Upon heating in protic solvents **18** is formed therefrom. The *S*-vinyl-compounds **1e** and **10** react in the crystalline state with $Cl_2$ gas at low temperatures in apparently clean reactions, even though the labile products could only be characterized by $^1$H-NMR spectra but decomposed upon usual purification procedures.




SCHEME 6

(d) Methylthiol is a useful reagent in organic gas/solid-additions and -substitutions and there may be some uses for atmospheric detoxification. The additions may proceed thermally or under the influence of light, but a prediction which combinations will be reactive is not possible. Sometimes thioethers may be more readily prepared via gas/solid-substitution.

The crystalline *S*-vinyl ether **14**, the product of the Reppe-vinylation of 2,3-dihydro-2-phenyl-1,5-benzothiazepine-4(5H)-one (see Experimental), adds methylthiol at 40°C relatively slowly to give the bis-thioether **20** in an *anti*-Markovnikov-type orientation. On the other hand, the liquids **1e** and **10** have to be crystallized at −45 or −30°C where they do not react in the dark at lower pressure (<0.2 bar in order to prevent condensation). However, **1e** reacts photochemically to give the *anti*-Markovnikov-product **21**, whereas **10** is stable even upon illumination. Also in benzene, **10** does not add $CH_3SH$ (3d, 20°C). The *anti*-Markovnikov orientation might be somehow enforced by crystal effects, or else this may point to radical mechanisms.



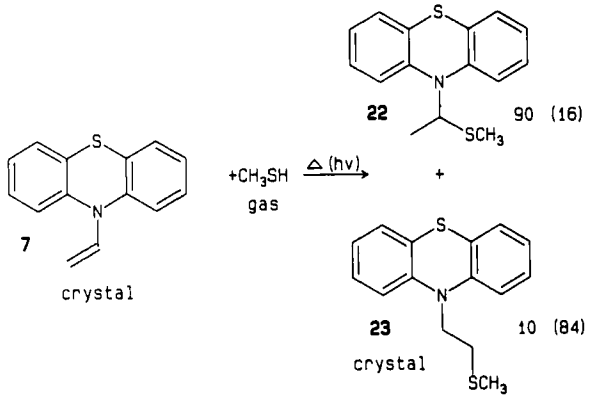

SCHEME 7

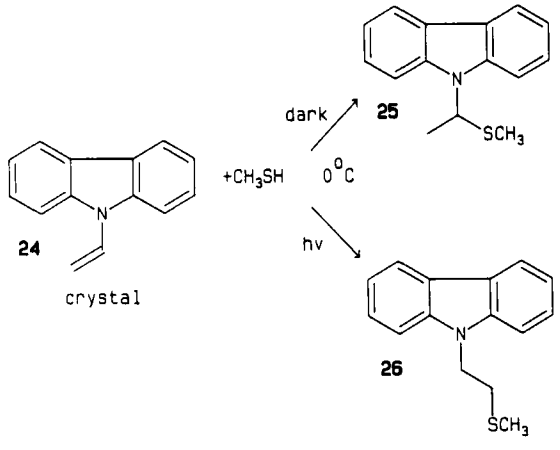
Some crystalline *N*-vinyl compounds are more reactive towards $CH_3SH$ than **14**, **1e** and **10**. Thus, **7** and **24** react at room temperature to give the Markovnikov-products **22** (overwhelmingly) and **25** (exclusively) (Scheme 8). This is what would be expected for an ionic addition mechanism, of course. **25** is also formed if **24** reacts with $CH_3SH$ in benzene. Most interestingly, we get different products, if the gas/solid-addition is performed under illumination. Now the *anti*-Markovnikov-products **23** or **26** prevail considerably. It appears, that radical chain mechanisms occur under these conditions and this would give a reasonable explanation of the complete regiospecifity in the case of **24/26** even though the light intensity will be smaller at the reaction sites towards the end of the reaction due to increased stray losses from the product crystals formed.

These are the first examples of gas/solid-reactions which show that different new solid phases can be formed depending on the reaction conditions, if those influence the addition mechanism. It is noteworthy that these additions to **7** and **24** run to completion even with deficient $CH_3SH$, down below the detection limit of the smell. The additions of $CH_3SH$ to *N*-vinylisatien have been published.[4]

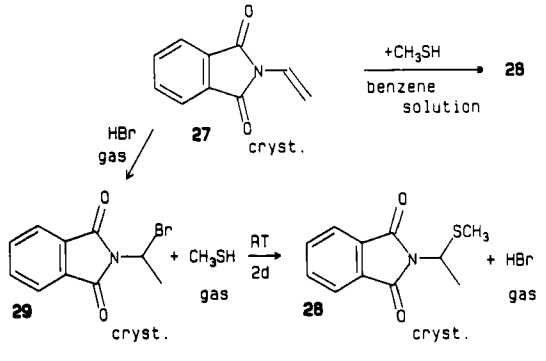
Of course, there are limits to gas/solid-additions of $CH_3SH$ because not all combinations are reactive. Thus, *N*-vinylphthalimide **27** could not be reacted under similar thermal or photochemical conditions, even though addition occurred in benzene solution to give **28**. However, there is an easier way to **28** via gas/solid-substitution, if HBr is added to crystalline **27** in the usual way[1,4,5] and highly reactive **29** is exposed afterwards to $CH_3SH$-gas. At relatively high conversion (70%) a clean substitution is encountered. These highly interesting substitutions with methylthiol are useful for the synthesis of elusive sulfur compounds. Thus, crystalline *N*-vinylpyrrolidone **30** does not add $CH_3SH$ gas at −40°C. However, if HBr is added first to give **31**[4] it is easy to obtain **32** by gas solid-substitution with $CH_3SH$.

(e) Sulfur dioxide is a highly interesting agent for organic gas/solid-reactions, because they may be helpful in solving the enormous problems which occur in the atmosphere. It has been reported recently,[6] that solid alkoxides react vigorously with $SO_2$-gas. In rather complicated transformations disulfites are formed. In an

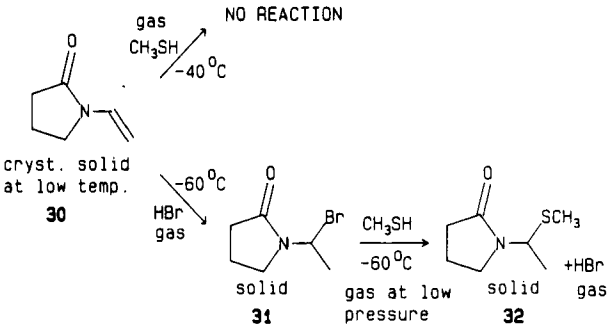


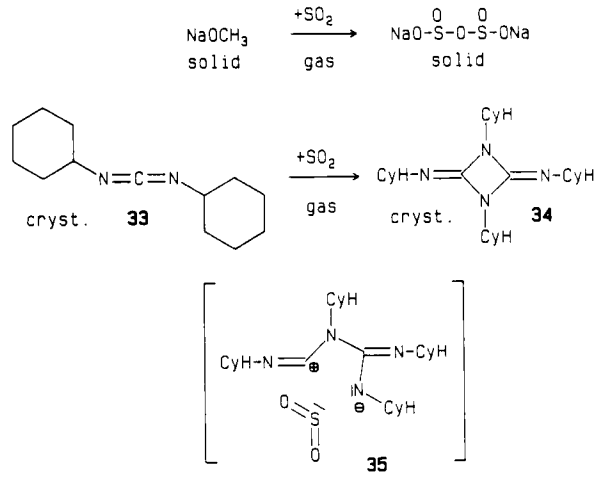

SCHEME 8




SCHEME 9




SCHEME 10




SCHEME 11

attempt to add $SO_2$ to solid dicyclohexylcarbodiimide **33** we found the first catalytic cyclodimerization in a gas/solid-reaction to give **34**, the formation of which we tentatively formulate via **35**. Undoubtedly there are several possibilities for intermediate attack of $SO_2$ to **33** and trapping of such intermediates by further **33** within the crystal lattice. Again the reaction is fast and complete. This is a very simple way to obtain the dimer **34**, which has been prepared previously by the action of $HBF_4$ in $CH_2Cl_2$ upon **33**.[7]

## CONCLUSIONS

Gas/solid-techniques are very useful in organic preparative sulfur chemistry, even though they are largely unrecognized, yet. Medium to large scale runs may be performed particularly easily and rapidly. This is beneficial for the production of highly reactive intermediates or hydrolytically sensitive compounds (e.g. **5**, **6**, **16**, **19**, **29**, **31**). Frequently, the properties of the product crystals are superior to those that had been treated with solvent (e.g. **2**). As solvents are avoided, this new technique is particularly considerate with respect to the available resources.

Of course, there might be important applications in atmospheric chemistry (e.g. $CH_3SH$, $SO_2$, HX).

The mechanism of organic gas/solid-reactions is largely unknown. As there are crystal transformations involved,[1,4] the crystal structures appear to help not very much in the prediction of gas/solid-reactivity. If low melting eutectica occur, cooling down is required. Anyhow, it appears favorable, if the product crystals have high melting points (e.g. **2**, **34**). The photoresults with **7** and **24** point to surface mechanisms with "peeling effects", which create fresh unblocked surface for further efficient attack by the gas, once it started, rather than host/guest-type mechanisms. Further work will have to be done in order to explain and advance this new potential in sulfur chemistry.

## EXPERIMENTAL

*Starting materials.* All starting materials were prepared according to the cited procedures. No special treatment was given to the crystals, except grinding wherever possible.

*Spectroscopy.* FTIR-spectra: Perkin-Elmer 1720; NMR-spectra: Bruker WP 300; UV-spectra: Perkin-Elmer-551S; mass spectra: Finnigan-MAT-212.

*General procedure.* 1 to 5 mmoles of the starting crystals (liquids are mixed with the double weight of glass Raschig coils and cooled down well below their melting points until they appear to be completely crystalline) are evacuated in round bottomed flasks (250 to 1000 ml) at the desired temperature. The reacting gas is added from a commercial high pressure bottle through a vacuum line against a safety valve. After completion of the reaction, excess gas is evacuated and the product analyzed.

*2-Alkyl(Aryl)-benzothiazoliumchlorides(bromides)* (**2a–e**); *benzoxazoliumchloride(bromide)* (**15**): 1 g of crystalline **1** or **10** are reacted with 22 mmol of HCl or HBr in a 500 ml flask under the conditions of Table I, to give the solid salts **2** which are analyzed by titration with 0.1 n NaOH against phenolphthaleine.

*(E)-2-(1,2-Diphenylethenyl)benzothiazole* (**3**): To 1.0 g (3.8 mmol) **2b** in 150 ml of dry $CH_2Cl_2$ are added 400 mg (3.8 mmol) benzaldehyde. After 5 h reflux the solvent is evaporated and the residue separated by prep. layer chromatography (200 g $SiO_2$, $CH_2Cl_2$) under exclusion of light. 510 mg (43%) **3** are eluted and recrystallized from methanol. Analytic and spectroscopic data in Reference 2.

*N-vinylsaccharin* **4** is synthesized according to a literature procedure,[8] purified by chromatography ($SiO_2$, $C_6H_6$/EtOAc = 4:1) and sublimation,[5] m.p. 129°C. $^1$H-NMR: see Reference 5.

*Adducts* **5** and **6**: 1.0 g (4.8 mmol) of **4** in an evacuated 500 ml flask are exposed to 1 bar of HCl or HBr (22 mmol) or connected to an evacuated flask with 2.0 g (12.5 mmol) $Br_2$ and put aside for two days. The excess gases are evaporated from the transformed crystals and the highly sensitive products analyzed by $^1$H-NMR in dried $CDCl_3$.

**5.** (X = Cl). $^1$H-NMR (80 MHz, $CDCl_3$): $\delta$ [ppm] = 2.26 (3H, d, $J$ = 7 Hz), 6.32 (1H, q, $J$ = 7 Hz), 7.7–8.2 (4H, arom.).

**5.** (X = Br). $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 2.43 (3H, d, $J$ = 7.0 Hz), 6.45 (1H, q, $J$ = 7.0 Hz), 7.85–7.98 (3H, arom.), 8.08–8.15 (1H, arom.).

**6.** $^1$H-NMR (80 MHz, $CDCl_3$): $\delta$ [ppm] = 4.03 (1H, ABX, $J$ = 11.6; 4.8 Hz), 4.73 (1H, BAX, $J$ = 11.6; 10.5 Hz); 6.19 (1H, XAB, $J$ = 10.5; 4.8 Hz), 7.7–8.2 (4H, arom.).

*N*-vinylphenothiazine **7** is obtained by Reppe-vinylation.[3]

TABLE I

Reaction conditions and analytical data of **2a–2e**, **15**

| Base (mmol) | Temp. [°C] | Time [h] | Salt **2** (%) (HBr) | (HCl) | $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm][a] |
|---|---|---|---|---|---|
| **1a**[3] (6.7) | −30 | 20 | 98 | 99 | 8.07–8.00 (1H), 7.87–7.80 (1H), 7.53–7.43 (1H), 7.43–7.33 (1H), 2.92 (s, 3H) (hydrobromide) |
| **1b**[3] (4.4) | −40 | 18 | 102 | 101 | 8.29–8.23 (1H), 7.93–7.86 (1H), 7.68–7.29 (7H), 4.82 (s, 2H) (hydrochloride) |
| **1c**[3] (4.7) | 20 | 20 | 103 | 102 | 8.87–8.80 (1H), 8.57–8.47 (2H), 8.05–7.98 (1H), 7.78–7.58 (5H) (hydrobromide) |
| **1d**[b] (5.5) | −10 | 4 | 99 | 100 | 8.15–8.09 (1H), 7.92–7.86 (1H), 7.60–7.51 (1H), 7.51–7.42 (1H), 3.02 (s, 3H) (hydrochloride) |
| **1e**[3] (5.2) | −45 | 3 | 98 | 99 | 8.46–8.40 (1 H), 7.93–7.86 (1 H), 7.73–7.65 (1 H), 7.61 (1H, $J$ = 14.2; 6.6 Hz), 6.97 (1 H, $J$ = 14.2; 0.5 Hz); 6.22 (1 H, $J$ = 6.6; 0.5 Hz) (hydrobromide) |
| **10** (5.6) | −30 | 3 | 95 | 100 | 8.03–7.97 (1 H), 7.69–7.63 (1 H), 7.60–7.50 (2 H), 7.26 (1H, $J$ = 12.6; 8.4), 6.16 (1 H, $J$ = 12.6; 0.7), 6.12 (1H, $J$ = 8.4; 0.7) (hydrobromide) |

[a] Due to strong concentration dependences, the NH signals are not listed here.
[b] Aldrich Chemie, Steinheim.



Reppe-vinylations[3] were performed in a shakeable electrically heated steel-autoclave of 500 ml content. The air was displaced by repeated initial shaking of the content (NH-, SH-compound, solvent, catalyst) with 20 bar of Ar and expansion down to 1 bar prior to the addition of acetylene well above its triple point at 20–25°C. The peak pressures are between 17 and 25 bar. For workup excess gas is expanded and flushed away with Ar, the solvent evaporated and the product isolated after extraction from the catalyst and chromatography or distillation (addition of some phenothiazine) and crystallization.

**1e.** $C_9H_7NS_2$ (193.3) calc. C 55.93 H3.65 N7.25 found C55.64 H3.25 N7.66; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 5.69 (1H, ABX, $J$ = 6.6; 0.5 Hz), 5.71 (1H, BAX, $J$ = 14.2; 0.5 Hz), 7.00 (1H, XAB, $J$ = 14.2; 6.6 Hz), 7.23–7.32 (1H, arom.), 7.36–7.45 (1H, arom.), 7.69 – 7.75 (1H, arom.), 7.86–7.92 (1H, arom.); MS (70 eV): $m/e$ = 193 (40%, $M^{+\cdot}$), 192 (100%), 167 (11%, M—$C_2H_2$), 149 (7%), 148 (6%), 135 (6%), 122 (4%).

**7.**[3] $^1$H-NMR (300 MHz, $D_6$-acetone): $\delta$ [ppm] = 4.18 (1H, ABX, $J$ = 9.3; 0.7 Hz), 4.76 (1H, BAX, $J$ = 15.6; 0.7 Hz), 6.93 (1H, XAB, $J$ = 15.6; 9.3 Hz), 7.09–7.15 (2H, arom.), 7.27–7.34 (4H, arom.), 7.42–7.45 (2H, arom.).

**10.** $C_9H_7NOS$ (177.2) calc. C61.00 H3.98 N7.90 found C60.61 H3.64 N8.15; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 5.66 (1H, ABX, $J$ = 8.4; 0.7 Hz), 5.69 (1H, BAX, $J$ = 12.6; 0.7 Hz), 7.03 (1H, XAB, $J$ = 12.6; 8.4 Hz), 7.16–7.29 (2H, arom.), 7.38–7.44 (1H, arom.), 7.57–7.63 (1H, arom.); MS (70 eV): $m/e$ = 177 (66%, $M^{+\cdot}$), 176 (100%), 151 (23%, M—$C_2H_2$), 133 (10%), 122 (20%), 91 (15%).

**12.** $C_8H_9NS$ (151.2) calc. C63.54 H9.26 N6.00 found C62.49 H9.59 N5.55; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 4.2 (2H, br.s, $NH_2$), 4.96 (1H, ABX, $J$ = 12.5; 0.5 Hz); 5.18 (1H, BAX, $J$ = 8.0; 0.5 Hz), 6.30 (1H, XAB, $J$ = 12.5; 8.0 Hz), 6.63–6.73 (2H, arom.), 7.10–7.20 (1H, arom.), 7.32–7.38 (1H, arom.); MS (70 eV): $m/e$ = 151 (84%, $M^{+\cdot}$), 150 (24%), 136 (100%, M—NH), 124 (14%), 118 (12%), 117 (13%).

TABLE II

Reaction conditions in high pressure vinylations

| Educt (mmol) | Solvent (ml) | Catalyst (g) | Acetylene [mmol] | Temp [°C] | Time [h] | Workup | Product (yield %) | m.p. (b.p./torr) |
|---|---|---|---|---|---|---|---|---|
| **8** (130) | DMAA[a] (150) | ZnO/Zn $(OAc)_2$ (3.0/1.0) | 440 | 180 | 8 | distill. | **1e** (64) | 118–120°C, 0.001 |
| PHT[b] (100) | dioxane (150) | K (0.25) | 440 | 120 | 24 | cryst. (EtOH) | **7**[3] (14) | 76–77°C, |
| **9** (132) | dioxane (150) | KOH (1.0) | 440 | 170 | 3.5 | distill. | **10** (63) | 82°C, 0.001 |
| **11** (160) | dioxane (150) | KOH (1.0) | 440 | 170 | 3 | distill. | **12** (37) | 82°C, 0.001 |
| **13** (16.5) | DMAA (150) | ZnO/Zn $(OAc)_2$ (3.0/1.0) | 220 | 180 | 30 | chrom. ($SiO_2$/PhH/EtOAc) | **14** (45) | 83–85°C |

[a] *N,N*-dimethylacetamide; [b] phenothiazine.

**14.** $C_{17}H_{15}NOS$ (281.4) calc. C72.57 H5.37 N4.98 found C72.92 H5.65 N4.78; IR (KBr): $\tilde{\nu}$ [$cm^{-1}$] = 3226 (NH), 1661, 1628 (C=O); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 4.98 (1H, ABX, $J$ = 13.0; 0.6 Hz), 5.27 (1H, BAX, $J$ = 7.8; 0.6 Hz), 6.32 (1H, XAB, $J$ = 13.0; 7.8 Hz), 6.54 (1H, AB, $J$ = 12.0 Hz), 7.06–7.16 (1H, arom.), 7.33–7.47 (4H, arom.), 7.50–7.60 (3H, arom.), 7.73 (1H, BA, $J$ = 12.0 Hz), 8.3 (1H, br.s, NH), 8.54–8.61 (1H, arom.); MS (70 eV): $m/e$ = 281 (13%, $M^{+\cdot}$), 236 (7%), 222 (17%, M—$SC_2H_3$), 204 (10%, M—$C_6H_5$), 190 (16%), 151 (19%), 136 (28%), 131 (100%), 103 (77%), 77 (50%).

Bis-thioether **20**: 200 mg (0.71 mmol) of crystalline **14** in a 250 ml flask at 40°C are exposed to 1 bar $CH_3SH$ for 5d. $^1$H-NMR analysis shows 76% conversion to **20**. This is separated from unreacted **14** by prep. layer chromatography ($SiO_2$/$CH_2Cl_2$) and crystallized from $CCl_4$; m.p. 106–107°C.

$C_{18}H_{19}NOS_2$(329.5) calc. C65.62 H5.81 N4.25 found C65.45 H5.81 N4.17; $^1$H-NMR (80 MHz, $CDCl_3$): $\delta$ [ppm] = 2.07 (3H, s), 2.5–2.75 (2H, AA'BB'), 2.9–3.15 (2H, BB'AA'), 6.67 (1H, AB, $J$ = 12.2 Hz), 6.95–7.2 (1H, arom.), 7.25–7.7 (7H, arom.), 7.78 (1H, BA, $J$ = 12.2 Hz), 8.5–8.65 (1H, arom.), 8.9 (1H, br.s, NH); MS (70 eV): $m/e$ = 282 (6%, M—$SCH_3$), 255 (71%), 236 (6%), 222 (5%), 131 (100%), 103 (68%); MS (CI, i-butane): 330 ($M + H^+$).

*Action of $CH_3SH$ upon* **1e** *and* **9**: 0.30 g **1e** (1.6 mmol) or **9** (1.7 mmol) in an evacuated 500 ml flask are crystallized and exposed at −45°C or −30°C, resp. with 0.3 bar of $CH_3SH$. After 24 h the gas is evaporated. $^1$H-NMR analysis shows only unreacted starting material.

0.50 g **1e** (2.6 mmol) or **9** (2.8 mmol) are exposed to $CH_3SH$ as above but with illumination through the cooling bath (Pyrex, $CH_3OH$) with a 500 W tungsten lamp or a Hanau 150 W high pressure mercury burner for 5 h. Only in the case **1e** there are conversions of 15 and 25% into **21**, which is isolated as an oil by prep. tlc.

**21.** $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 2.24 (3H, s), 2.92–2.99 (2H, AA'BB'), 3.54–3.61 (2H, BB'AA'), 7.28–7.32 (1H, arom.), 7.38–7.45 (1H, arom.), 7.74–7.79 (1H, arom.), 7.83–7.88 (1H, arom.).

*Addition of HCl to* **14**. 0.30 (1.07 mmol) of crystalline **14** are treated with 1 bar of HCl in a 500 ml flask for 2 h at room temperature. Excess gas is evacuated, 10 ml of $CH_3OH$ condensed in under high vacuum and reacted for 1 h at room temperature. The solvent and HCl formed are distilled off in a closed system under high vacuum and the lightbrown residue analyzed by $^1$H-NMR-spectroscopy. When **17** is tried to be recrystallized from protic solvents, there is formation of **18**.[9]

**17.** $^1$H-NMR (80 MHz, $CDCl_3$): $\delta$ [ppm] = 1.43 (3H, d, $J$ = 4.8 Hz), 3.43 (3H, s), 4.73 (1H, q, $J$ = 4.8 Hz), 6.47 (1H, AB, $J$ = 12.2 Hz), 6.9 – 7.9 (8H, arom.), 7.76 (1H, BA, $J$ = 12.2 Hz), 8.5–8.6 (1H, arom.), 8.9 (1H, br.s, NH).

*Action of $Cl_2$ to* **1e** *and* **10**. 0.5 g of **1e** (2.6 mmol) or **10** (2.8 mmol) in a 500 ml flask are added to 2 g of Raschig coils from glass and crystallized at −45°C. 0.5 bar of $Cl_2$ (11 mmol) are let in. After 5 h excess gas is evaporated and the yellow solid product analyzed by $^1$H-NMR.

**19.** (X = S). $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 4.11 (1H, ABX, $J$ = 12; 6 Hz), 4.22 (1H, BAX, $J$ = 12; 6 Hz), 6.19 (1H, XAB, $J$ = 6; 6 Hz); 7.35–7.53 (2H, arom.), 7.78–8.01 (2H, arom.).

**19.** (X = O). $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 4.13 (1H, ABX, $J$ = 12; 6 Hz), 4.20 (1H, BAX, $J$ = 12; 6 Hz), 6.12 (1H, XAB, $J$ = 6; 6 Hz), 7.21 – 7.38 (2H, arom.), 7.42–7.70 (2H, arom.).

*Addition of $CH_3SH$ to crystalline* **7**. 0.40 g (1.8 mmol) **7**[3] in a 250 ml flask are exposed to 0.9 bar of $CH_3SH$ (10 mmol) at room temperature and put aside for 2 d. $^1$H-NMR analysis of the solid obtained indicates a mixture of 90% **22** and 10% **23**.

If the same run is done under illumination with a 500 W tungsten lamp for 11 h, the yield is 16% **22** and 84% **23**.

Due to its easy decomposition into phenothiazine upon chromatography at $SiO_2$ **22** could not be obtained in pure form, whereas **23** survived: dec.p. 240°C.

**22.** $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 1.57 (3H, d, $J$ = 7.0 Hz), 2.10 (3H, s), 3.80 (1H, q, $J$ = 7.0 Hz), 6.83–7.18 (8H, arom.).

**23.** $C_{15}H_{15}NS_2$ (273.4) calc. C65.90 H5.53 N5.12 found C69.61 H5.68 N4.90.

$^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 2.19 (3H, s), 2.86–2.95 (2H, AA'BB'), 4.04–4.13 (2H, BB'AA'), 6.81–7.20 (8H, arom.); MS (CI, i-butane): $m/e$ = 274 ($M + H^+$).

*Addition of $CH_3SH$ to crystalline* **24**. 1.0 g (5.2 mmol) **24**[3] in an evacuated 500 ml flask are exposed to 0.9 bar of $CH_3SH$ (20 mmol) at room temperature and in the dark for 18 h. There is complete reaction to give solid **25**, m.p. 105–106°C (from *n*-hexane). If deficient $CH_3SH$ is applied (2.6 mmol), the stench disappears completely and **25** is formed.

1.0 g (5.2 mmol) **24** in a 500 ml flask with 0.9 bar of $CH_3SH$ (20 mmol) are illuminated at 0°C with a 500 W tungsten lamp for 2 h. There is complete conversion into **26**; m.p. 64°C (from i-propanol).

**25.** $C_{15}H_{15}NS$ (241.4) calc. C74.65 H6.26 N5.80 found C74.36 H6.25 N5.77; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 1.76 (3H, s), 1.94 (3H, d, $J$ = 6.9 Hz), 5.97 (1H, q, $J$ = 6.9 Hz), 7.21–7.27 (2H, arom.), 7.40–7.47 (2H, arom.), 7.63–7.76 (2H, arom.), 8.05–8.12 (2H, arom.); MS (70 eV): $m/e$ = 241 (15%, $M^{+\cdot}$), 194 (100%, M—$SCH_3$), 193 (37%), 192 (20%), 167 (18%), 166 (11%), 140 (8%).

**26.** $C_{15}H_{15}NS$ (241.4) calc. C74.65 H6.26 N5.80 found C74.89 H6.19 N5.68; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 2.10 (3H, s), 2.88–2.96 (2H, AA'BB'), 4.47–4.55 (2H, BB'AA'), 7.18–7.28 (2H, arom.), 7.37–7.50 (4H, arom.), 8.04–8.11 (2H, arom.); MS (70 eV): $m/e$ = 241 (32%, $M^{+\cdot}$), 194 (3%, M—$SCH_3$), 180 (100%), 152 (12%).

If 250 mg (5.2 mmol) $CH_3SH$ are added to 500 mg (2.6 mmol) of **24** in 10 ml benzene, a quantitative yield of **25** is obtained after 48 h.

*N-1-(thiomethyl)ethylphthalimide* (**28**):
(a) To 200 mg (1.2 mmol) **27** in 10 ml benzene are added 100 mg (2.1 mmol) $CH_3SH$. The solution is heated to 40°C for 50 h under reflux. 150 mg (59%) **28** are formed ($^1$H-NMR analysis) and separated by prep. tlc on $SiO_2$ with $CH_2Cl_2$.
(b) 1.0 g (3.9 mmol) freshly prepared **29**[5] in a 500 ml flask are exposed to 0.5 bar $CH_3SH$ (11 mmol) at room temperature for 2d. There is 70% conversion to **28**. This is separated by prep. tlc (basic $SiO_2$, $C_6H_6$/EtOAc = 4:1) from decomposing **29**; m.p. 72–73°C (from *n*-hexane); $C_{11}H_{11}NO_2S$ (221.3) calc. C59.71 H4.82 N6.33 found C59.54 H4.85 N6.09; $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 1.87 (3H, d, $J$ = 7.1 Hz), 2.16 (3H, s), 5.45 (1H, q, $J$ = 7.1 Hz), 7.71–7.78 (2H, arom.), 7.82–7.89 (2H, arom.); MS (70 eV): $m/e$ = 221 (7%, $M^{+\cdot}$), 174 (100%, M—$SCH_3$), 147 (23%), 130 (24%).

*N-1-(thiomethyl)ethylpyrrolidone-(2)* **32**. According to Ref. 4 1.0 g (9.0 mmol) **30** are reacted in a 500 ml flask at −60°C with HBr gas, to give quantitatively **31**.[4] Excess HBr is evaporated and the evacuated cooled (−60°C) flask connected to a 1l flask which had been charged under vacuum with 0.3 bar of $CH_3SH$ (13.4 mmol). After 19 h, all gases are evacuated and the crystals which soften above −30°C are chromatographed at basic $SiO_2$ with EtOAc, to give an oily fraction of 600 mg **32**.

$^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 1.38 (3H, d, $J$ = 7.1 Hz), 1.96 (3H, s), 1.99–2.10 (2H), 2.39–2.48 (2H), 3.26–3.37 (1H), 3.52–3.63 (1H), 5.47 (1H, q, $J$ = 7.1 Hz).

*1,3-Dicyclohexyl-2,4-bis(cyclohexylimino)-1,3-diazetidine* **34**. 1.0 g (4.8 mmol) crystalline **33** (Fa. Fluka Chemie AG, Buchs) are exposed to 1 bar of $SO_2$ in a 500 ml flask at 0°C for 21 h. The excess gas is pumped off. A quantitative yield of the dimer **34**, m.p. 115–118°C (Ref. 7: 122.5°C), is obtained. IR(KBr): $\tilde{\nu}$ = 1684 cm$^{-1}$ (C=N); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ [ppm] = 3.45–3.27 (1H), 3.27–3.07 (1H), 2.03–1.37 (10H), 1.37–1.00 (10H); $^{13}$C-NMR (75.5 MHz, $CDCl_3$): $\delta$ [ppm] = 147.41 (2 C=N), 56.06 (2C), 55.43 (2C), 34.92 (4C), 30.33 (2C), 25.94 (2C), 25.69 (4C), 25.42 (4C), 24.72 (4C); MS (CI, i-butane): $m/e$ = 413 ($M + H^+$).

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