7. The Chemistry of Stable Carbenes

Part 2[1])

Benzoin-Type Condensations of Formaldehyde Catalyzed by Stable Carbenes

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Stable carbenes derived from thiazole, 1*H*-imidazole, and 4*H*-1,2,4-triazole are efficient catalysts for benzoin-type condensations of formaldehyde. Catalysts derived from *N*-substituted thiazolium salts trimerize formaldehyde to dihydroxyacetone (**II**). Catalysts based on 1,4-disubstituted 4*H*-1,2,4-triazol-1-ium salts give glycolaldehyde (**I**) as the main product and no **II**, whereas *N*,*N*′-disubstituted 1*H*-imidazol-3-ium salts yield mixtures of both products. The isolation of several intermediates in the catalytic cycle provide a better insight into the reaction mechanism.

Introduction. – The cyanide-catalyzed condensation of benzaldehyde to benzoin was serendipitously discovered by *Liebig* and *Wöhler* [1] in 1832 upon treating bitter almond oil (a mixture of benzaldehyde and HCN) with KOH. The scope of this cyanide-catalyzed benzoin condensation proved to be quite narrow, since aromatic aldehydes with strong electron-donating or -withdrawing substituents do not react under these conditions [2].

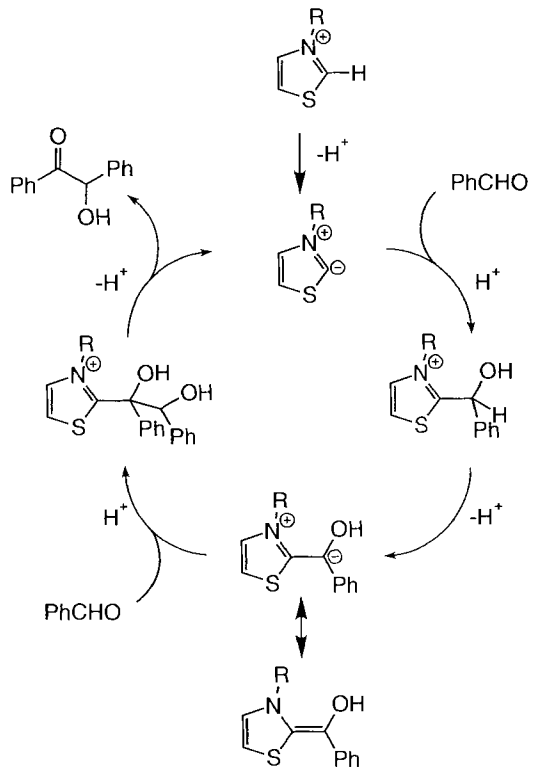
It took over one hundred years until *Ukai et al.* [3] accidentally discovered that this reaction can also be catalyzed by 3-ethylthiazolium bromide in the presence of base. *Breslow* [4] showed in the course of his investigations on the mechanism of this reaction, that thiamine (vitamin B_1, a naturally occurring thiazolium salt) was able to catalyze the decarboxylative condensation of pyruvic acid to acetoin as well as the benzoin condensation of benzaldehyde. The proposed mechanism for the benzoin condensation is shown in *Scheme 1*.

Stetter et al. [5] were the first to recognize the potential of 3-alkylthiazolium salts as catalysts for the benzoin-type condensation of aliphatic aldehydes which cannot be condensed with cyanides.

The first report on 3-alkylthiazolium-salt-catalyzed condensation of formaldehyde was published in 1980 by *Castells* and coworkers [6]. The use of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride and Et_3N in dimethylformamide (DMF) at 100° provided a complex mixture of C_5- and C_6-carbohydrates as products. This reaction was

[1]) Part 1: [15].

Scheme 1. *Mechanism Proposed by* Breslow *for the Thiazolium-Salt-Catalyzed Benzoin Condensation*



further optimized by *Inoue* and coworkers [7]. They condensed formaldehyde with *N*-ethylbenzothiazolium bromide and Me_3N as catalysts and obtained dihydroxyacetone (= 1,3-dihydroxypropan-2-one; **II**) in yields of up to 70%.

The basic features of the mechanism of thiazolium-catalyzed reactions were elucidated by *Breslow* in 1958 [4]. Recently, *Castells* and coworkers postulated '2,2′-bithiazolinylidenes' (= 2,3-dihydro-2-(thiazol-2(3*H*)-ylidene)thiazol) to be the actual catalytically active species, which should be formed through the known dimerization of the respective thiazolium ylides upon treatment of the thiazolium salt with base [8]. In 1994, *Breslow* and *Kim* reported NMR investigations and kinetic measurements which render the participation of dimers in the catalytic cycle unlikely [9]. This interpretation was confirmed by *Jordan* and coworkers [10] who examined the mechanism of the benzoin reaction *via* isotope labelling. These recent publications demonstrate that the details of azolium-salt catalysis are still subject to controversy.

The combination of a thiazolium salt and a base can be regarded as a precursor to thiazol-2-ylidenes (= thiazol-1-ium-2-ides), a so-called 'stable' or 'nucleophilic carbene'. Precursors to other different types of 'nucleophilic carbenes', as *e.g.* 2,2′-bi(1,3-dialkylimidazolidinylidenes) [11], *N*,*N*′-disubstituted 2,2′-bithiazolylidenes [8], and 1,3,4-thiadia-

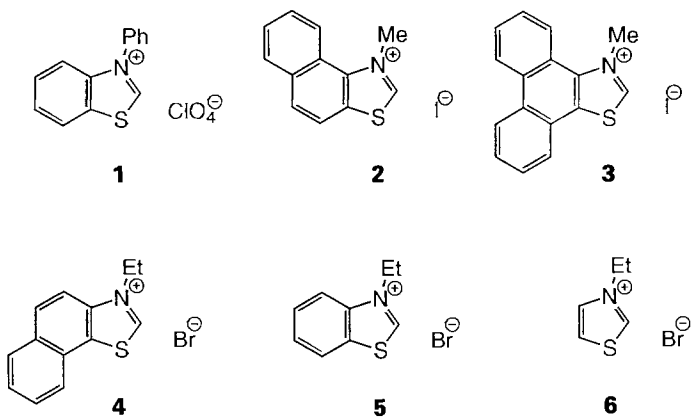
zolium salts/Et_3N [12], were also examined as catalysts for the benzoin condensation. Although several 'stable carbenes' of the 1,3-disubstituted imidazol-2-ylidene (= 1*H*-imidazol-3-ium-2-ide) [13] [14] and 1,4-disubstituted 1,2,4-triazol-5-ylidene (= 4*H*-1,2,4-triazol-1-ium-5-ide) [15] type were recently isolated and characterized, tests concerning their catalytic activity were never reported to date.

On an industrial scale, methane, the main component of natural gas, can easily be converted to formaldehyde. An efficient catalytical condensation of formaldehyde to dihydroxyacetone (**II**) or to glycolaldehyde (= hydroxyacetaldehyde; **I**) would thus provide a route to C_2- and C_3-chemicals from methane, but no catalysts were ever described that can selectively condense formaldehyde to glycolaldehyde.

In this work, we describe attempts to improve the known catalysts for the synthesis of dihydroxyacetone and new catalysts which selectively condense formaldehyde to glycolaldehyde. Furthermore, we report the isolation of intermediates of the catalytic formaldehyde condensation, contributing to the mechanistic discussion of azolium-salt-catalyzed reactions. The selectivity of the formaldehyde condensation using different heterocyclic catalysts will be discussed on the base of high-level *ab initio* calculations.

Results and Discussion. – *Condensation of Formaldehyde with Thiazolium-Type Catalysts. N*-Alkyl-substituted benzothiazolium salts were already used by *Inoue* and coworkers [7b] to catalyze the coupling of formaldehyde to dihydroxyacetone (**II**). They showed that the nature of the alkyl group (Me, Et, and i-Pr) had no effect either on the activity or on the selectivity of the catalyst but did not investigate the effect of substituents on the benzene ring.

To establish a structure-activity relationship, we synthesized 3-phenylbenzothiazolium perchlorate (**1**), 1-methylnaphtho[1,2-*d*]thiazolium iodide (**2**), and 3-methylphenanthro[9,10-*d*]thiazolium iodide (**3**) and compared their catalytical activity with the already known 3-ethylnaphtho[2,1-*d*]thiazolium bromide (**4**), 3-ethylbenzothiazolium bromide (**5**), and 3-ethylthiazolium bromide (**6**). These catalysts were tested by treating 40 equiv. of formaldehyde (as a paraformaldehyde suspension in dimethylformamide



1 **2** **3**

4 **5** **6**

Table 1. *C–C Coupling of Formaldehyde Catalyzed by Various Thiazolium Salts*

Catalyst	Yield [%]			
	glyceraldehyde (**I**)	dihydroxyacetone (**II**)	C_4-carbohydrates	higher carbohydrates[b])
1	2.0	15.0	27.6	+
2	1.9	27.8	28.7	–
3	[a])	27.0	13.8	–
4	[a])	84.7	2.4	+
5	1.3	64.8	9.7	–
6	[a])	22.2	12.4	–

[a]) Not determined. [b]) +/–: C_5 and C_6 carbohydrates formed/not formed.

(DMF)) with 1 equiv. each of thiazolium salt and Et_3N at 100° for 1 h. *Table 1* shows the product yields as determined by gas chromatography after oximation and silylation (see also *Fig. 1*).

Dihydroxyacetone (**II**) is always the major product, except whith catalyst **1** where C_4-carbohydrates predominate. These C_4-carbohydrates consist mainly of erythrulose (**IV**) with only small amounts of other isomers (*e.g.* **V** and **VI**). Glyceraldehyde (= 2,3-dihydroxypropanal; **III**) and higher carbohydrates (C_5 and C_6) are formed only as minor products. Glycolaldehyde (**I**) is either not formed at all or at most in traces (yield *ca.* 0.2% with catalyst **5**).

Changing the substituent at the N-atom of the catalyst from Et to Ph causes a decrease in the activity and a shift in the product spectrum towards higher carbohydrates (*cf.* **1** and **5** in *Table 1*). A possible explanation for this behavior is the inductive destabilization of the intermediate carbene by the Ph groups which probably leads to increased dimerization and thus reduces the number of catalytically active species despite the enhanced acidity of the thiazolium salt[2]). Phenyl rings condensed onto the thiazole

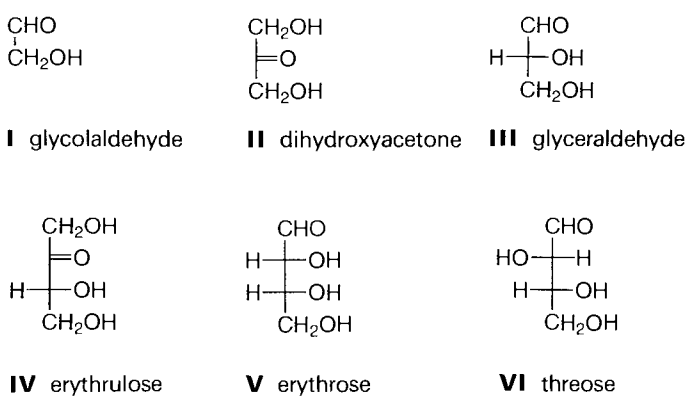
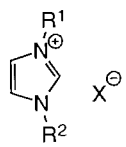


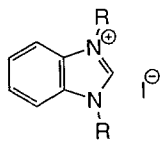
Fig. 1. *Products of the catalytic C–C coupling of formaldehyde* (for chiral substrates only the D-form is shown)

[2]) A very low activity in the benzoin reaction was also observed for Ph-substituted thiazolium salts such as 3,4,5-triphenylthiazolium perchlorate [16].

ring increase both the catalyst activity and dihydroxyacetone selectivity (*cf.* **6**, **5**, and **4**). This increased activity is probably due to an increased kinetic acidity of the thiazolium salt. The reported values for the second-order rate constants of the OH^--catalyzed H/T exchange are $6 \cdot 10^4$ $M^{-1}s^{-1}$ for a *N*-benzylthiazolium salt and $1.8 \cdot 10^6$ $M^{-1}s^{-1}$ for a *N*-benzylbenzothiazolium salt [17]. A similar increase in acidity would be expected when going from a benzo- to a naphthothiazolium salt. The catalytic activity of **4** is indeed greater than that of **5**, but this is not true for **2** and **3**. In **2** and **3** (and also in **1**), the substituent at the N-atom is sterically congested by the other substituents of the thiazole ring, and this may lead to the decreased catalytic activity.

Condensation of Formaldehyde with Imidazolium-Type Catalysts. N,N'-Disubstituted imidazolium salts have never been reported as catalysts for the C–C coupling of aldehydes, but the related 1,1',3,3'-tetraalkyl-2,2'-biimidazolinylidenes were shown to catalyze the coupling of benzaldehyde to benzoin [11] [18]. To test the catalytic activity of imidazolium salts, a number of representative compounds were synthesized and tested as above (formaldehyde/catalyst 40:1, Et_3N as base, DMF as solvent, 1 h at 100°). The following substances were synthesized and tested: 1-Butyl-3-methyl-1*H*-imidazol-3-ium iodide (**7**), 1,3-di(*p*-tolyl)-1*H*-imidazol-3-ium chloride (**8**), 1,3-diethyl-1*H*-benzimidazol-3-ium iodide (**9**), and 1,3-diphenyl-1*H*-benzimidazol-3-ium iodide (**10**).





7 R^1 = Me, R_2 = Bu, X = I
8 $R^1 = R^2$ = *p*-Tolyl, X = Cl

9 R = Et
10 R = Ph

With the exception of 1-butyl-3-methyl-1*H*-imidazol-3-ium bromide (**7**), all catalysts are active (see *Table 2*). The salts **8** and **9** produce mainly C_4- and higher carbohydrates, together with some dihydroxyacetone (**II**) and glyceraldehyde (**III**). Catalyst **10** is the most active among the tested imidazolium salts and also gives the best dihydroxyacetone selectivity. This catalyst is also remarkable, because it produces some glycolaldehyde (**I**).

Table 2. *C–C Coupling of Formaldehyde Catalyzed by Various Imidazolium Salts*

Catalyst	Yield [%]				
	glycolaldehyde (**I**)	glyceraldehyde (**III**)	dihydroxy-acetone (**II**)	C_4-carbo-hydrates	higher carbohydrates[a])
7	0.0	0.0	0.0	0.6	–
8	0.8	0.3	5.1	15.7	+
9	0.0	0.7	1.5	15.5	+
10	4.2	2.5	33.9	17.2	+

[a]) +/–: C_5- and C_6-carbohydrates formed/not formed.

As a rule, imidazolium catalysts are all less active than thiazolium salts. This is probably due to the lower kinetic acidity of imidazolium salts as compared to thiazolium salts. As in the case of the thiazolium salts, the catalyst activity correlates nicely with the kinetic acidities. The second-order rate constants for the base-catalyzed H/D exchange in imidazolium salts are smaller by a factor of *ca.* 100 than for thiazolium salts. Reported values are $2.0 \cdot 10^2$ $M^{-1}s^{-1}$ for 1,3-dimethyl-1*H*-imidazol-3-ium iodide and $4.3 \cdot 10^4$ $M^{-1}s^{-1}$ for 1,3-dimethyl-1*H*-benzimidazol-3-ium chloride [19]. Although no experimental measurements are available, an increase in kinetic acidity is expected when the substituents at the N-atom are changed from alkyl to aryl. Accordingly, the aryl-substituted catalysts (**8** and **10**) are more active than their alkyl-substituted counterparts (**7** and **9**). Since 'imidazolin-ylidenes' do not dimerize as readily as the corresponding 'thiazolin-ylidenes' [13] [14], the increased acidity due to the electron-withdrawing substituents directly translates to enhanced catalytic activity. As in the case of the thiazolium salts, the condensation of a benzene ring increases both the kinetic acidity and the catalytic activity (compare **7** with **9** and **8** with **10**).

Condensation of Formaldehyde with 1,2,4-Triazolium-Type Catalysts. The kinetic acidity of 1-ethyl-4-phenyl-4*H*-1,2,4-triazolium chloride was also reported in the literature [19]. The H/D exchange, with a second-order rate constant of $8.6 \cdot 10^7$ $M^{-1}s^{-1}$, is almost two orders of magnitude faster than in 3-benzylbenzothiazolium chloride [17], and one could then expect 1,2,4-triazolium salts to be very active catalysts for the C–C coupling of formaldehyde, which is indeed the case. When a 10 wt.-% suspension of paraformaldehyde containing 2.5 mol-% of Et_3N is treated with 2.5 mol-% of a thiazolium salt (*e.g.* **5**) at 100°, it will take *ca.* 30–60 min for the paraformaldehyde to completely dissolve and for the solution to become clear. If one uses 2.5 mol-% of a 1,2,4-triazolium salt instead (*e.g.* 1,3,4-triphenyl-4*H*-1,2,4-triazol-1-ium perchlorate (**11**; see below and *Fig. 2* for structure in the solid state), it will take no more than a few seconds for the solution to turn clear. To obtain acceptable reaction times, the 1,2,4-triazolium salts are tested at 80 instead of 100° and with 0.5 instead of 2.5 mol-% catalyst. The 1,2,4-triazolium-salt catalysts are not only much more active than their imidazolium and thiazolium counterparts, but they also give different products. With catalysts of the triazolium type, glycolaldehyde (**I**) is the major product together with some glyceraldehyde (**III**) and higher carbohydrates, but almost no dihydroxyacetone (**II**). Using the above mentioned reaction conditions and **11** as catalyst, and after a reaction time of 10 min, a mixture of **I** (59%), **III** (10%), C_4-carbohydrates (2%), and **II** (0.2% yield) is obtained. The C_4-carbohydrates are probably formed *via* competing aldol reactions of the starting materials and the products, respectively. While catalysts of the thiazolium salt type yield almost exclusively erythrulose (**IV**; aldol of **II** and formaldehyde), the 1,2,4-triazolium salt catalysts give approximately equal amounts of threose and erythrose (self aldol of **I**).

Structure-Activity Relationships for 1,2,4-Triazolium Catalysts. The catalytic C–C coupling of formaldehyde to glycolaldehyde (**I**; a C_2 product) is, from our point of view, more interesting than the conventional coupling to dihydroxyacetone (**II**; a C_3 product)[3]). A great deal of effort was therefore spent optimizing the structure of 1,2,4-triazolium

[3]) The bulk price for the conventional C_2 raw material ethene is on average 1.2–1.5 times higher than the price of the C_3 raw material prop-1-ene.

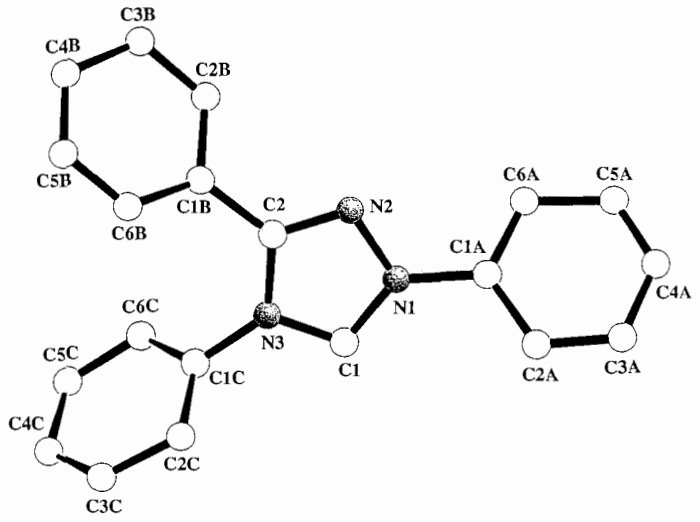


Fig. 2. *Structure of* **11** *in the solid state* (SCHAKAL representation; arbitrary numbering). Selected structural parameters (Å, °): N(1)–C(1) 1.35(1), N(1)–N(2) 1.38(1), N(2)–C(2) 1.31(1), N(3)–C(1) 1.32(1), N(3)–C(2) 1.36(1); C(1)–N(1)–N(2) 109.5(9), C(2)–N(2)–N(1) 103.7(9), C(1)–N(3)–C(2) 106.2(9), N(3)–C(1)–N(1) 108.3(9), N(2)–C(2)–N(3) 112(1), C(1)–N(3)–C(1C)–C(2C) 59(1), C(1)–N(1)–C(1A)–C(2A) –32(2).

catalysts to increase the activity and decrease the amount of by-products. As will be shown below, the catalyst activity is strongly dependent on the catalyst structure, but the selectivities remain unchanged. Typical product yields as a function of the reaction time are shown in *Fig. 3*. This time dependence of the yields is typical for all the 1,2,4-tria-

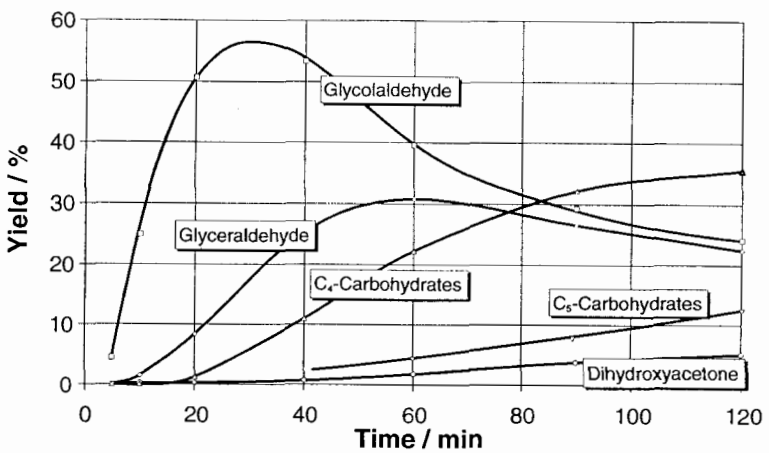
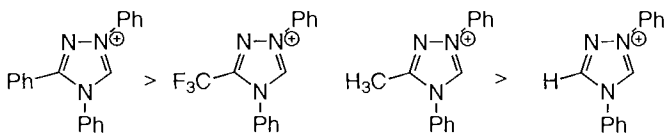


Fig. 3. *Time dependance of the product yields in the C–C coupling of formaldehyde catalyzed by* **11** *and* Et_3N (initial concentration of formaldehyde: 10%, DMF as solvent, 0.5 mol-% each of **11** and Et_3N). Higher carbohydrates were determined only semiquantitatively.

zolium-type catalysts tested and is due to the fact that glycolaldehyde (**I**), glyceraldehyde (**II**), threose (**VI**), and erythrose (**V**) are themselves aldehydes and as such can undergo benzoin-type condensations or base-catalyzed aldol reactions.

The pseudo-second-order rate constant for the coupling, computed as minus the rate of conversion of formaldehyde (extrapolated to $t = 0$) divided by the catalyst concentration, is used as a measure of the catalyst activity. All measurements with 1,2,4-triazolium salts are made using a suspension of 10 wt.-% formaldehyde (as paraformaldehyde) in DMF at 80° and 0.5 mol-% each of catalyst and Et_3N.

Effect of Substituents at Position 3 of 1,2,4-Triazolium-Type Catalysts. The substituents at position 3 have a very strong influence on the catalyst activity, but this influence seems to be only of sterical nature. As shown in *Fig. 4*, a Ph substituent leads to the most active catalyst (**11**). The catalysts with a Me (**13**) or a CF_3 (**12**) substituent have comparable activities and are only somewhat less active than **11**. Catalyst **14** with a H-atom at position 3 is much less active.

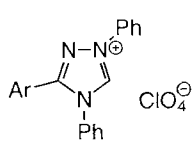


11 **12** **13** **14**

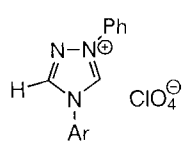
$4.4\ M^{-1}s^{-1}$ $1.1\ M^{-1}s^{-1}$ $0.64\ M^{-1}s^{-1}$ $0.08\ M^{-1}s^{-1}$

Fig. 4. *Pseudo-second-order rate constants for the C–C coupling of formaldehyde by 1,2,4-triazolium-type catalysts with different substituents at position 3*

The activity of the catalyst seems to be determined solely by the bulk of the substituent at position 3, since catalysts with substituents like Me and CF_3, with very different electron-donating abilities but similar sizes, have comparable activities. Also, replacement of the Ph group at position 3 of **11** by *para*-substituted aryl groups, gives catalysts with comparable activities regardless of the electronic properties of the substituents (4-$MeOC_6H_4$ (**15**), 4-ClC_6H_4 (**16**), and 4-$NO_2C_6H_4$ (**17**) were tested).



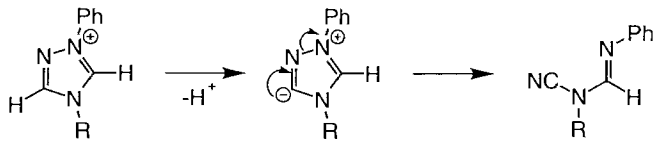
14 Ar = H
15 Ar = 4-$MeOC_6H_4$
16 Ar = 4-ClC_6H_4
17 Ar = 4-$O_2NC_6H_4$



18 Ar = 4-FC_6H_4
19 Ar = 4-MeC_6H_4
20 Ar = 4-$O_2NC_6H_4$
21 Ar = 4-$MeOC_6H_4$
22 Ar = 3-ClC_6H_4
23 Ar = 2,6-$Me_2C_6H_3$

The low activity of catalysts unsubstituted at position 3 is independent of the nature of the substituent at position 4. A series of 1-phenyl-4-aryl-4*H*-1,2,4-triazolium perchlorates (Ar = Ph (**14**), 4-FC_6H_4 (**18**), 4-MeC_6H_4 (**19**), 4-$NO_2C_6H_4$ (**20**), 4-$MeOC_6H_4$ (**21**), 3-ClC_6H_4 (**22**), and 2,6-$Me_2C_6H_3$ (**23**)) were tested. The measured pseudo-second-order rate constants are all equal within the limits of experimental error (0.08 $M^{-1}s^{-1}$). This surprisingly low reactivity is probably due to the low stability of triazolium salts unsubstituted at C(3) under basic conditions, since treatment with base leads to the removal of the acidic H–C(3) with subsequent formation of the respective *N*-cyanobenzamidines *via* ring opening, resulting in the irreversible destruction of the catalyst (*Scheme 2*). In some cases the *N*-cyanobenzamidine could be isolated and characterized.

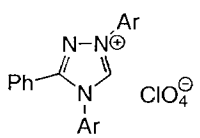
Scheme 2. *Deactivation of Triazolium Salts Unsubstituted in Position 3* via *Ring Opening*



Effect of Condensed Rings at Positions 3 and 4 of 1,2,4-Triazolium-Type Catalysts. A series of condensed triazolium-type catalysts were also synthesized and tested. The results are shown in *Fig. 5*. Catalysts **24**–**26** have all similar activities, comparable to those of catalyst **13**. As previously observed with the thiazolium-type catalysts, the condensation of further benzene rings has a beneficial effect on the activity (*cf.* **25** and **26**). However, when the condensed rings possess a *peri*-H-atom, as shown for **27** and **28**, the activity decreases considerably. A possible explanation for this lower catalytic activity may be sterical hindrance between the *peri*-H-atoms and the catalyst-bound aldehyde. This interpretation is in accordance with the observation that the Ph rings of the active catalyst **11** are twisted out of the heterocyclic plane (see *Fig. 2*) [15].

Effect of Substituents at Positions 1 and 4 of 1,2,4-Triazolium-Type Catalysts. Two catalysts with substituents other than Ph at positions 1 and 4 were synthesized and tested. The 1,4-bis(3,5-dichlorophenyl)-3-phenyl-4*H*-1,2,4-triazol-1-ium perchlorate (**29**) has a pseudo-second-order rate constant of 1.2 $M^{-1}s^{-1}$ which is *ca.* 1/3 to 1/4 that of the triphenyl-substituted catalyst **11**. In contrast, 1,4-bis(2,6-dimethylphenyl)-3-phenyl-4*H*-1,2,4-triazol-1-ium perchlorate (**30**) is completely inactive, probably due to steric hindrance.

Preparation of Dihydro-methoxy-triazoles and -imidazoles. The perchlorates **11**, **15**–**17**, and **29** react with NaOMe in MeOH at room temperature to produce the corresponding 4,5-dihydro-1,3,4-triaryl-5-methoxy-1*H*-1,2,4-triazoles **31**–**35** [15] (*Scheme 3*). According to the same pattern, 1,3-diphenyl-1*H*-benzimidazol-3-ium iodide (**10**) reacts to produce 2,3-dihydro-2-methoxy-1,3-diphenyl-1*H*-benzimidazole (**36**).



29 Ar = 3,5-$Cl_2C_6H_3$
30 Ar = 2,6-$Me_2C_6H_3$

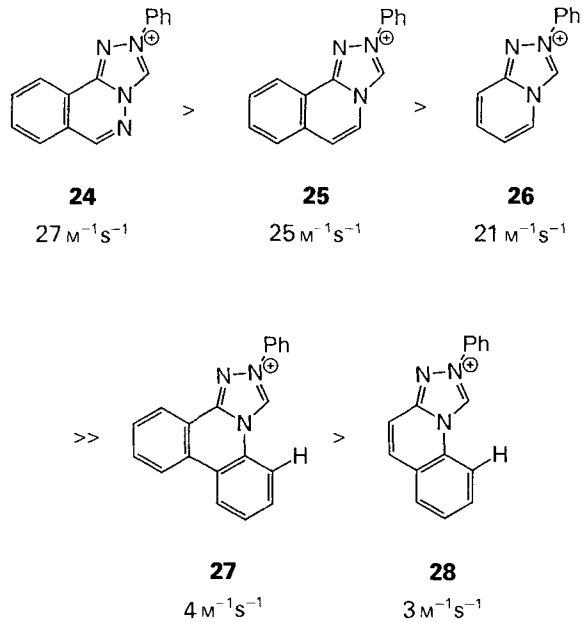
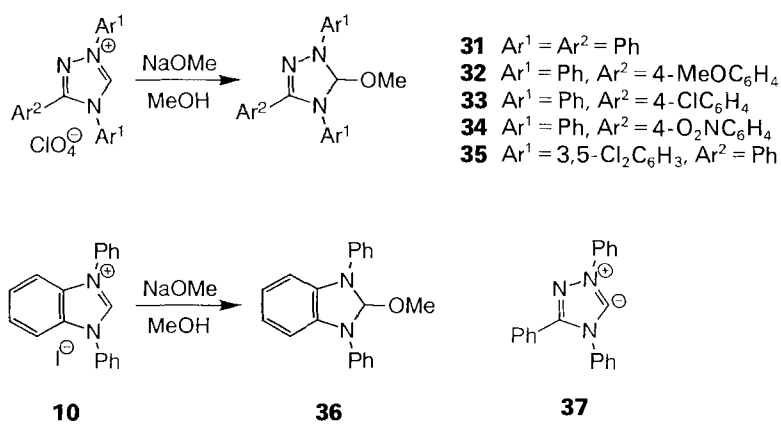


Fig. 5. *Pseudo-second-order rate constants for the C–C coupling of formaldehyde by 1,2,4-triazolium-type catalysts with rings condensed at positions 3 and 4*

Base-Free Catalysts. A common problem to all the above described thiazolium-, imidazolium-, and triazolium-type catalysts, besides their low solubility in common organic solvents, is the necessity of adding a base as cocatalyst. If care is not taken to avoid excess base, it can induce an unselective, autocatalytic coupling of formaldehyde to higher linear and branched carbohydrates [20]. As we previously showed [15], 4,5-dihy-

Scheme 3. *MeO-Addition Products of 1,2,4-Triazolium and Benzimidazolium Salts*



dro-5-methoxy-1,3,4-triphenyl-1*H*-1,2,4-triazole (**31**) will thermally decompose above 90° into MeOH and 1,3,4-triphenyl-4*H*-1,2,4-triazol-1-ium-5-ide (**37**)[4]), which is the same product expected from the deprotonation of **11** [13]. Indeed, **31** proved to be an excellent catalyst for the C–C coupling of formaldehyde. The pseudo-second-rate constant measured in a 10 wt.-% suspension of paraformaldehyde in DMF at 80° with 0.05 mol-% **31** is 41 $M^{-1}s^{-1}$ (*cf.* 4.4 $M^{-1}s^{-1}$ for **11**). This means that **31** is almost one order of magnitude more active than the combination of **11** and Et_3N.

A further increase in activity can be obtained by using directly the nucleophilic carbene **37** [15] as the catalyst. The measured pseudo-second-order rate constant in 2-methylbutan-2-ol as solvent at 80° is 46 $M^{-1}s^{-1}$. Since selectivities remain unchanged, this increase in activity usually does not justify the effort of preparing the nucleophilic carbene **37**.

The 2,3-dihydro-2-methoxy-1,3-diphenyl-1*H*-benzimidazole (**36**) also thermally eliminates MeOH although not as cleanly and at a much higher temperature than **31**[4]). Nevertheless, it is a much more active catalyst (0.4 $M^{-1}s^{-1}$ at 80°) than the corresponding imidazolium salt **10** with Et_3N (0.2 $M^{-1}s^{-1}$ at 100°). As expected, the product selectivities obtained with **36** and with **10**/Et_3N (see *Table 2*) as catalysts are almost identical.

Influence of Reaction Parameters on the Performance of Catalyst **31**. Dihydromethoxy-triazole **31** is a very active catalyst for the C–C coupling of formaldehyde to glycolaldehyde (**I**), but unfortunately the selectivity is limited by the fact that it will also catalyze the reaction of **I** with formaldehyde and with itself to produce higher carbohydrates. Besides the catalyst structure, some other parameters influence both the activity and the selectivity of this catalyst. In contrast to the triazolium salts, **31** is soluble in most organic solvents, even in unpolar ones, so solvent effects could easily be studied.

The influence of the solvent on the catalytic activity of **31** was much smaller than expected and not always easy to interpret. With AcOEt, tetrahydrofuran (THF), *t*-BuOH, and 2-methylbutan-2-ol as solvents, the pseudo-second-order rate constants are approximately the same as in the standard solvent DMF (*ca.* 41 $M^{-1}s^{-1}$). Lower reaction rates are observed in 2-ethylhexan-1-ol, propanenitrile (both *ca.* 12 $M^{-1}s^{-1}$), MeOH, and toluene (both *ca.* 6 $M^{-1}s^{-1}$). Almost no catalytic activity is observed, when H_2O is used as solvent. The highest activity is observed with 1,2-dimethoxyethane (*ca.* 53 $M^{-1}s^{-1}$) and 3-methylpentan-3-ol (*ca.* 59 $M^{-1}s^{-1}$).

Solvents have only a very small influence on the selectivities. The only exception are primary and secondary alcohols. For aprotic solvents and tertiary alcohols, the variation of the glycolaldehyde (**I**) selectivity with the formaldehyde conversion is independent of the solvent. A typical curve is shown in *Fig. 6* for the tertiary alcohol 2-methylbutan-2-ol. When primary or secondary alcohols are used as solvents, the glycolaldehyde selectivity decreases faster with increasing formaldehyde conversion (see *Fig. 6*). By forming acetals and hemiacetals, alcohols reduce the effective concentration of the aldehydes present. But since acetals and hemiacetals of formaldehyde are more stable than those of **I**, the reduction in the effective concentration of formaldehyde will be greater than that of **I**. This will favor side reactions involving **I**.

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[4]) Weight loss (differential thermogravimetry, heating rate 2°/min): 9.4% between 90 and 115° from **31** (9.7% expected for loss of MeOH) and 8.1% between 175 and 220° from **36** (10.6% expected for loss of MeOH).

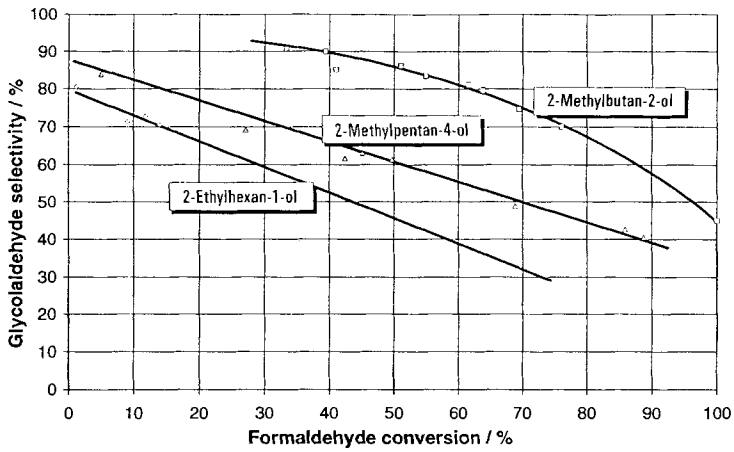


Fig. 6. *Glycolaldehyde* (**I**) *selectivity as a function of formaldehyde conversion for a primary* (2-ethylhexan-1-ol), *a secondary* (2-methylpentan-4-ol), *and a tertiary alcohol* (2-methylbutan-2-ol) *as solvent*

This interpretation is supported by the observation that the glycolaldehyde (**I**) selectivity increases with increasing formaldehyde concentration. Within the range of 10 to 50% formaldehyde conversion, the glycolaldehyde selectivity will increase by 8% when increasing the initial formaldehyde concentration from 8.9 to 15 wt.-% (homogeneous solution in 2-methylpentan-4-ol).

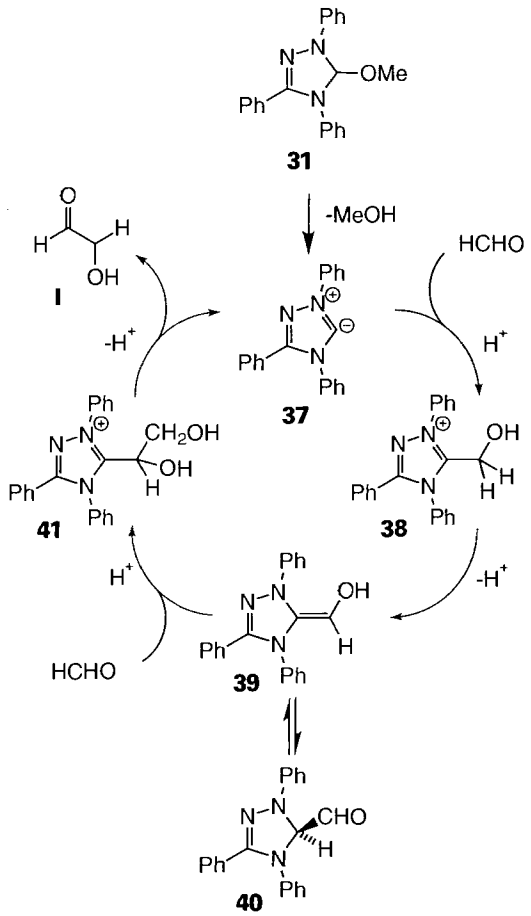
Changes in temperature in the range 60–100° or changes in the catalyst concentration have no effect on the glycolaldehyde selectivity. The reaction rate increases markedly with temperature, but the catalyst will also deactivate faster. If care is taken to exclude H_2O and O_2, an increase in temperature will increase the overall turnover number of the catalyst. In a pilot plant, where H_2O- and O_2-free solutions of formaldehyde in 3-methylpentan-3-ol could be continuously prepared and catalytically coupled, 0.004 mol-% of **31** were enough to achieve a formaldehyde conversion of 60% with a glycolaldehyde selectivity of *ca.* 85% (catalyst turnover: *ca.* 14000 mol formaldehyde converted per mol catalyst).

Compared to thiazolium catalysts, **31** is much less H_2O- and O_2-sensitive. If lower turnover numbers can be accepted, the catalyst will still work well with air-saturated solvents containing up to 1% of H_2O. Glycolaldehyde (**I**) can be isolated from the 3-methylpentan-3-ol solution by extraction with H_2O. H_2O and unreacted formaldehyde can be removed by stripping with superheated steam. The crude **I** still contaminated with glyceraldehyde (**III**) and higher carbohydrates can be isolated by vacuum distillation. Although this method is quite appropriate for pilot-plant scale (over 100 kg of **I** were produced this way), it is not easily adaptable for the laboratory-scale synthesis of **I**.

The use of **31** as a catalyst for the coupling of higher aldehydes will be reported in a separate paper.

Reaction Mechanism. Our proposed mechanism for the benzoin-type condensation of formaldehyde to glycolaldehyde (**I**) is shown in *Scheme 4*. This mechanism is similar to the one first proposed by *Breslow* [4] for the thiazolium-salt-catalyzed condensation of benzaldehyde to benzoin (see *Scheme 1*).

Scheme 4. *Proposed Mechanism for the Benzoin-Type Condensation of Formaldehyde to Glycolaldehyde* (**I**) *Catalyzed by* **31**

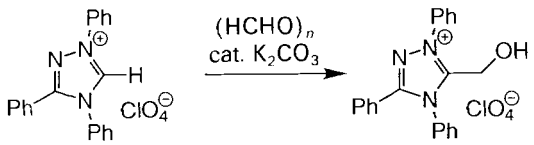


The generation of the catalytically active carbene **37** by thermal decomposition of precursor **31** was already described in detail [15]. As already mentioned above, carbene **37** can also be isolated and directly used as the catalyst. Carbene **37** behaves similarly to the stable imidazolium carbenes of *Arduengo et al.* [13] [14] in that it forms no dimers in solution. This is in contrast with thiazolium ylides and 1,3-disubstituted tetrahydroimidazol-2-ylidenes [11] [18] [21–26] for which only the dimers were characterized. The fact that **37** forms no dimers but still is much more active a catalyst than the thiazolium ylides makes the participation of dimers in the catalysis highly improbable. This view is completely in accordance with the most recent studies on the thiazolium-catalyzed benzoin condensation [9] [10].

In the first step of the catalytic cycle, the nucleophilic carbene **37** adds to formaldehyde with concomitant protonation, forming 5-(hydroxymethyl)triazolium salt **38**. It was

possible to isolate **38** by running the reaction in dioxane or THF with triazolium salt **11** as the catalyst and using only 0.1–0.2 mol-% of K_2CO_3 as base instead of the equimolar amount of Et_3N (*Scheme 5*). If the reaction was stopped before all the paraformaldehyde was consumed, **38** could be isolated in yields up to 65%.

Scheme 5. *Synthesis of 5-(Hydroxymethyl)triazolium Salt* **38**

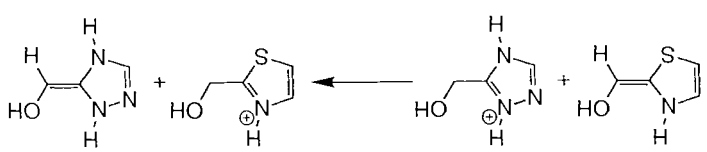


11 **38**

The catalytic activity of **38** is within the experimental error equal to that of **11**, in agreement with the mechanism of *Scheme 4*[5]). The formation of (α-hydroxybenzyl)-thiazolium salts as stable intermediates in the benzoin condensation was demonstrated by NMR [9] [10], and (hydroxymethyl)thiazolium salts were synthesized and characterized [27] [28], but such intermediates were never isolated from the base-catalyzed reaction of a catalytically active azolium salt with an aldehyde itself.

In the next step, **38** must be deprotonated at C(α) to form enol **39** (only one of the two possible (*E*/*Z*) isomers is shown; see *Scheme 4*). Under the reaction conditions, these two enols will most probably equilibrate with aldehyde **40**. *Ab initio* calculations at the (MP2/TZP//HF/SVP) level for these three species show, as expected, the aldehyde to be the most stable species. The enols with the OH group *cis* and *trans* to N(1) lie 58.3 and 56.4 kJ/mol higher in energy than aldehyde **40**[6]). All attempts to isolate **39** or **40** by deprotonation of **38** failed. However, in the case of a 2-(hydroxymethyl)-3-methylbenzo-thiazolium salt, base-catalyzed H/D exchange at C(α) was demonstrated [28] and its rate

Scheme 6. *Homodesmal H–C(α) Exchange Between a Thiazolium and a 1,2,4-Triazolium Catalyst*



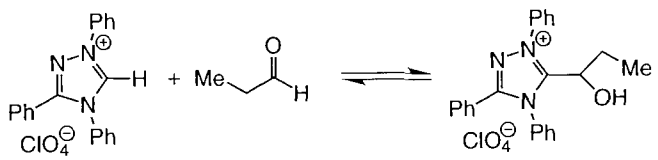
[5]) This hydroxymethylation was also attempted with a benzothiazolium salt but without success. However, 2-(hydroxymethyl)-3-methylbenzothiazolium iodide, independently synthesized by the reaction of 2-lithio-3-methylbenzothiazole with formaldehyde followed by *N*-methylation with MeI, proved to be as effective a catalyst as **5**.

[6]) As a comparison, at the (MP2/TZP//HF/SVP) level of theory, the enol form of acetaldehyde (vinyl alcohol) lies 79.6 kcal/mol higher in energy than acetaldehyde.

estimated to be 10^4 times slower than the H/D exchange at C(2) of thiazolium salts [29]. The homodesmal H–C(α) exchange of *Scheme 6* is calculated at the (MP2/TZP//HF/SVP) level to be exothermic ($\Delta G = -15.6$ kJ/mol at 300 K), and thus 2-(hydroxymethyl)triazolium salts are expected to be considerably more acidic than the corresponding 2-(hydroxymethyl)thiazolium salts.

In the following step of the mechanism, enol **39** reacts with a further molecule of formaldehyde with concomitant protonation to give **41** (*Scheme 4*). Despite several attempts, **41** could be isolated neither from the reaction of **11** with glycolaldehyde (**I**) nor from the reaction of **38** with formaldehyde. However, **42** which is isoelectronic with **41** could easily be synthesized from **11** and propionaldehyde (*Scheme 7*).

Scheme 7. *Synthesis of the 5-(1-Hydroxypropyl)triazolium Salt* **42**



11 **42**

The last step in our proposed reaction mechanism calls for the cleavage of **41** into glycolaldehyde (**I**) and **11**. This would correspond to the reverse of the reaction in *Scheme 7*, and indeed this reaction proved to be reversible. The equilibrium constants at different temperatures could easily be determined by heating *ca.* 0.2M **42** in (D_6)DMSO in a sealed NMR tube until the concentrations no longer changed. The measured equilibrium constants are shown in *Table 3*. Plotting the logarithm of the equilibrium constant against the reciprocal of the absolute temperature gives a straight line. From its slope, a ΔH of −46.2 kJ/mol for the forward reaction in *Scheme 7* can be obtained[7]). Although the benzoin condensation is known to be a reversible reaction, this is, to our knowledge, the first instance in which the reversibility of a single step in the catalytic cycle is observed.

The nature of the final product obtained on condensing formaldehyde with different catalysts can easily be understood in terms of the energy required to release the product aldehyde from the catalyst. An intermediate like **41** can either eliminate glycolaldehyde

Table 3. *Equilibrium Constants for the Reaction of* **11** *with Propionaldehyde to Give* **42** (K = [**11**][EtCHO]/[**42**])

Temp. [°C]	77.8	99.6	108.8	125.0
K [mol l^{-1}]	0.195	0.473	0.679	1.293

[7]) The reaction enthalpy and entropy are calculated at the (MP2/TZP//HF/SVP) level of theory: ΔH_R (298 K) = −71.3 kJmol^{-1} and ΔS_R (298 K) = −191.5 Jmol^{-1}K^{-1}.

(**I**) or be α-deprotonated and react with a further mol of formaldehyde to produce finally dihydroxyacetone (**II**). The relative ease with which different types of catalysts eliminate **I** can be estimated by using the following homodesmal reaction:

$$X{-}R^+ + Y{:} \rightarrow X{:} + Y{-}R^+,$$

where X: and Y: can be 4,5-dihydro-1*H*-tetrazol-5-ylidene, 4,5-dihydro-1,3,4-thiadiazol-5-ylidene, 4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene, 2,3-dihydrothiazol-2-ylidene, or 2,3-dihydro-1*H*-imidazol-2-ylidene, and $X{-}R^+$ or $Y{-}R^+$ represent the corresponding azolium salts (R = H), (hydroxymethyl)azolium salts ($R = CH_2OH$), or (1,2-dihydroxyethyl)azolium salts ($R = CH(OH)CH_2OH$). The energy of thee homodesmal reactions is calculated *ab initio* at the (MP2/TZP//HF/SVP) level. The results using 1,2,4-triazolium as the reference system Y are shown in *Table 4*.

Table 4. *Calculated* ΔG (at 300 K, $kJmol^{-1}$) *for the Homodesmal Reactions* $X - R^+ + Y{:} \rightarrow X{:} + Y - R^+$

X	R = H	$R = CH_2OH$	$R = CH(OH)CH_2OH$
Tetrazolium	−68.6	−62.7	−60.9
1,3,4-Thiadiazolium	−22.3	−14.5	−16.3
1,2,4-Triazolium (Y)	0.00	0.00	0.00
Thiazolium	37.0	40.5	37.9
Imidazolium	61.7	58.0	56.3

Two interesting trends can be observed in the data of *Table 4*. First, the calculated relative thermodynamic acidities (row for R = H) give a fairly good ($r^2 = 0.977$) linear free-energy correlation with the measured second-order rate constants for the base-catalyzed H/D exchange of several azolium salts (1,4-diethyl-1*H*-tetrazolium: $2.9 \cdot 10^{11}$ $M^{-1}s^{-1}$ [19]; 1-ethyl-4-phenyl-4*H*-1,2,4-triazolium: $8.6 \cdot 10^7$ $M^{-1}s^{-1}$ [19]; 3-benzylthiazolium: $1.8 \cdot 10^4$ $M^{-1}s^{-1}$ [17]; 1,3-dimethyl-1*H*-imidazolium: $2.0 \cdot 10^2$ $M^{-1}s^{-1}$ [19]). Second, the exchange energies are almost independent of what is actually being exchanged: H^+, CH_2OH^+, or $CH(OH)CH_2OH^+$. If similar linear free-energy relationships hold for all three exchanges, then the rate of elimination of glycolaldehyde (**I**) will increase in the order: imidazolium < thiazolium < 1,2,4-triazolium < 1,3,4-thiadiazolium < tetrazolium. In the case of imidazolium- and thiazolium-type catalysts, the elimination of **I** becomes slower than the addition of a third formaldehyde to give dihydroxyacetone (**II**). This can react no further and will be then slowly cleaved. This interpretation thus easily explains the fact that catalysts which give **I** have faster reaction rates than those which yield **II**.

The authors wish to express their gratitude to the innumerable people at the Ammonia Laboratory of the *BASF AG* in Ludwigshafen who made this work possible. We particularly thank Dr. *Bernhard Knuth*, our project engineer, who was responsible for the miniplant, and Dr. *Carsten Gröning* for the synthesis of compound **24**. The work of *D. Enders* and *K. Breuer* was supported by the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft* (SFB 380, *Leibniz*-Preis).

Experimental Part

General. All reagents and solvents were obtained commercially and used as received, except for dimethylformamide (DMF) which was dried and stored over molecular sieves. GC: *Hewlett-Packard-5890A* gas chromatographs. M.p.: *HGW-SGV-500-Plus* melting-point apparatus with video monitoring; uncorrected. UV/VIS Spectra: *Hewlett-Packard-8451A* diode-array spectrophotometer; λ_{max} (E) in nm. IR Spectra: *Perkin-Elmer-882* scanning infrared spectrometer; in cm^{-1}. ^1H-, ^{13}C- and ^{19}F-NMR Spectra: at 25°; *Bruker-AMX-400* spectrometer at 400, 110.6, and 376.6 MHz, resp. *Bruker-AC-250* spectrometer at 250, 62.9, and 235.4 MHz, resp. δ in ppm, J in Hz. MS: chemical ionization (CI) and electron ionisation (EI) on *Finnigan-MAT-312* sector-field spectrometer at 70 eV with isobutane as the reactant for CI; fast-atom bombardment (FAB) MS on *Finnigan-MAT-90* sector-field spectrometer using Ar and nitrobenzyl alcohol or thioglycerin as matrix; electro-spray ionization (ESI) MS on *Finnigan-MAT-90* quadrupole spectrometer with flow-injection analysis. Differential scanning calorimetry/thermogravimetry: in the temp. range 30–300° with a heating rate of 2.0°/min under H_2 on an aluminium oxide sample holder using a *Metsch SCA 409* instrument. Elemental analyses were performed by the central analytical laboratory at *BASF*.

Standard Test for Thiazolium- and Imidazolium-Type Catalysts. Paraformaldehyde (2.8 g, 94 mmol), thiazolium salt (2.3 mmol), 3 Å molecular sieves (0.1 g), and dry DMF (10.0 g) were placed in a 25-ml glass autoclave with a small magnetic stirring bar and deaerated with an Ar stream for 10 min. Et_3N (0.23 g, 2.3 mmol) was then added with a syringe and the autoclave quickly closed under Ar and placed in a thermostated oil bath where it was stirred for 1 h at 100°. The autoclave was then quickly cooled in an ice bath and opened. A 0.5-g sample of reaction mixture was quenched with oximation reagent[8]) (10.0 g) and kept for 1 h at 70°. Then 1 ml of the oximated sample was mixed with hexamethyldisilazane (1 ml) and Me_3SiCl (1 ml) and left for 1 h at r.t. whereby pyridinium hydrochloride precipitated. The oximated and silylated sample was filtered with a disposable syringe filter (*Milipore*, 0.45 µm) and the clear filtrate analyzed by GC (0.2 µl sample, 30-m *DB5* column; temp. program: single ramp from 60 to 300° with a heating rate of 5°/min). This procedure for analysis of the products is a modification of that developed by *Anderle* [30].

Standard Test for Triazolium-Type Catalysts. Paraformaldehyde (2.0 g, 66 mmol), triazolium salt (0.33 mmol), and dry DMF (18.0 g) were placed in a 25-ml *Schlenk* tube with a small magnetic stirring bar and deaerated with an Ar stream for 10 min. Et_3N (35 mg, 0.35 mmol) was then added with a microliter syringe and the tube closed with a rubber septum and placed in a thermostated oil bath where it was stirred at 80°. Samples were taken at regular intervals (usually after 15, 30, 60, 120, 180, and 240 min) and quenched with the oximating reagent. Oximation, silylation, and GC analysis were performed as described above.

Standard Test for Base-Free Catalysts **31**–**36**. Paraformaldehyde (2.0 g, 66 mmol) and *t*-BuOH (18.0 g) were placed in a 25-ml *Schlenk* tube with a small magnetic stirring bar and deaerated with an Ar stream for 10 min. The catalyst (0.33 mmol) was then added and the tube closed with a rubber septum and placed in a thermostated oil bath where it was stirred at 80°. Samples were taken at regular intervals (usually after 15, 30, 60, 120, 180, and 240 min) and quenched with the oximating reagent. Oximation, silylation, and GC analysis were performed as described above.

3-Phenylbenzothiazolium Perchlorate (**1**). To a soln. of 2-(phenylamino)-benzenethiol [31] (7.0 g, 34.8 mmol) in HCOOH (120 ml), a few mg of Zn powder were added. The mixture was heated to reflux under Ar for 6 h and then left overnight at r.t. After removal of a small amount of precipitate, 10% perchloric acid (30 ml) was added to the filtrate, the mixture stirred for 5 min and diluted with H_2O (150 ml), and the precipitate filtered, washed once with H_2O, air-dried, washed twice with Et_2O, and dried *in vacuo*: 8.1 g (75%) of **1**. Colorless powder. M.p. 195–197°. ^1H-NMR (250 MHz, (D_6)DMSO): 10.9 (*s*, SCHN); 8.6 (*m*, 1 arom. H); 7.9 (*m*, 4 arom. H); 7.8 (*m*, 5 arom. H). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 165.9 (SCHN); 130.2, 126.2 (arom. CH, double intensity); 131.6, 130.1, 128.5, 125.2, 117.1 (arom. CH, single intensity); 141.2, 135.7, 131.1 (arom. C). Anal. calc. for $C_{13}H_{10}ClNO_4S$ (311.7): C 50.09, H 3.23, Cl 11.37, N 4.49, O 20.53, S 10.29; found: C 49.9, H 3.3, Cl 11.2, N 4.4, O 20.7, S 10.1.

1-Methylnaphtho[1,2-d]thiazolium Iodide (**2**). Naphtho[1,2-*d*]thiazole [32] (10.0 g, 54 mmol) and MeI (50 g, 350 mmol) were charged to a glass autoclave and stirred for 24 h at 100°. The residue obtained after distilling off the excess MeI was stirred with CH_2Cl_2 (150 ml) for 15 min. The solid product was collected by filtration and dried *in vacuo* to give 11 g (33.5 mmol, 62%) of **2**. Colorless crystals. M.p. 179–180°. ^1H-NMR (250 MHz, (D_6)DMSO):

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[8]) The oximation reagent consists of a soln. of hydroxylamine hydrochloride (70 g) in pyridine (1000 g) containing butane-1,4-diol (5.00 g) as an internal standard for GC.

10.5 (*s*, SCHN); 8.95 (*d*, 1 arom. H); 8.5 (*d*, 1 arom. H); 8.35 (*d*, 2 arom. H); 7.9 (*m*, 2 arom. H); 4.9 (*s*, Me). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 162.7 (SCHN); 129.9, 129.6, 128.6, 128.1, 122.3, 120.4 (arom. CH); 136.8, 133.2, 132.0, 122.9 (arom. C); 45.2 (Me). Anal. calc. for $C_{12}H_{10}INS$ (327.3): C 44.05, H 3.08, I 38.79, N 4.28, S. 9.8; found: C 44.0, H 3.1, I 38.6, N 4.3, S 10.0.

*3-Methylphenanthro[9,10-*d*]thiazolium Iodide* (**3**). Phenanthro[9,10-*d*]thiazole was prepared using the method of *Boggust et al.* [32] starting from phenanthrene-9-amine. The anal. data were identical with those reported in [33]. Phenanthro[9,10-*d*]thiazole (3.0 g, 12.7 mmol) and MeI (30 g, 211 mmol) were charged to a glass autoclave and stirred for 6 h at 100°. The residue obtained after distilling off the excess MeI was stirred with CH_2Cl_2 (30 ml) for 10 min. The solid product was collected by filtration and dried in air: 0.7 g (1.9 mmol, 15%) of **3**. Light-brown powder. M.p. 191–192°. ^{1}H-NMR (250 MHz, (D_6)DMSO): 10.7 (*s*, SCHN); 9.0 (*m*, 1 arom. H); 8.9 (*m*, 2 arom. H); 7.9 (*m*, 4 arom. H); 4.9 (*s*, Me). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 161.4 (SCHN); 129.7, 129.0, 128.9, 128.5, 128.4, 124.7, 124.6, 124.1 (arom. CH); 136.6, 132.2, 130.6, 123.8, 123.2, 121.8 (arom. C); 45.8 (Me). Anal. calc. for $C_{16}H_{12}INS$ (377.3): C 50.94, H 3.21, I 33.64, N 3.71, S 8.5; found: C 50.2, H 3.2, I 34.5, N 3.8, S 8.3.

*3-Ethylnaphtho[2,1-*d*]thiazolium Bromide* (**4**) was prepared as described in [22].

3-Ethylbenzothiazolium Bromide (**5**) was prepared as described in [22].

3-Ethylthiazolium Bromide (**6**) was prepared as described in [4].

*1-Butyl-3-methyl-1*H*-imidazol-3-ium Iodide* (**7**) was prepared as described in [34].

*1,3-Bis(4-methylphenyl)-1*H*-imidazol-3-ium Chloride* (**8**) was prepared as described in [35].

*1,3-Diethyl-1*H*-benzimidazol-3-ium Iodide* (**9**) was prepared as described in [36].

*1,3-Diphenyl-1*H*-benzimidazol-3-ium Iodide* (**10**) was prepared as described in [37].

*1,3,4-Triphenyl-4*H*-1,2,4-triazol-1-ium Perchlorate* (**11**) was prepared as described in [38] or [39] or according to the following procedure. HCOOH (60 ml) and *N*-phenylbenzamide phenylhydrazone [40] (5 g, 17.4 mmol) were heated for 18 h to 130° in a glass autoclave. Excess HCOOH was then distilled off *in vacuo* and the viscous residue digested with 10% perchloric acid (30 ml). The precipitate was filtered, washed with H_2O and recrystallized from abs. EtOH: 6.1 g (88%) of **11**. Colorless crystals. M.p. 238° (dec.). ^{1}H-NMR (250 MHz, (D_6)DMSO): 11.3 (*s*, NCHN); 8.1 (*d*, 1 arom. H); 7.7 (*m*, 13 arom. H). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 153.1 (NCHN); 132.2, 131.4, 130.7 (arom. CH, single intensity); 130.3, 130.1, 129.2, 129.1, 126.5, 120.6 (arom. CH, double intensity); 143.0, 134.8, 131.9, 122.3 (arom. C). FAB-MS (pos.): 298.2 (M^+). Anal. calc. for $C_{20}H_{16}ClN_3O_4$ (397.8): C 60.38, H 4.05, Cl 8.91, N 10.56, O 16.09; found: C 59.8, H 4.9, Cl 8.9, N 10.5, O 16.2.

X-Ray Structure Determination of **11**. Crystals of sufficient quality were obtained from EtOH at r.t. The compound crystallized in monoclinic space group $P2_1/c$ (No. 14), $a = 13.568(1)$, $b = 8.013(1)$, $c = 20.649(2)$ Å and $\beta = 91.481(8)°$. $V = 2244.4$ Å^3, $Z = 4$, and $M_r = 443.9$. The calculated density and the total number of electrons in the cell amounted to 1.314 gcm^{-3} and $F(000) = 928$, resp. $\theta_{max} = 75.2°$ for solution and refinement. The structure was solved by means of direct methods as implemented in the XTAL 3.2 package of crystallographic routines, employing GENSIN to generate structure-invariant relationships and GENTAN for the general tangent phasing procedure (GENSIN, GENTAN in XTAL 3.2, XTAL 3.2 reference manual (Eds. S. R. Hall, H. D. Flack, J. M. Stewart), Universities of Western Australia, Geneva, and Maryland, Lamb, Perth, 1992). A total number of 8460 reflections was collected in the range $-17 < h < 17$, $0 < k < 10$ and $-25 < l < 25$ at r.t. on an *Enraf-Nonius-CAD4* diffractometer, employing graphite monochromated CuK_α radiation ($\lambda = 1.54179$ Å), $\mu = 18.28$ cm^{-1}, no absorption correction, $\omega/2\theta$ scans, internal consistency $R_{av} = 0.03(5)$. Reflections (1876) with $I > 2\sigma(I)$ entered the final full-matrix least-squares refinement process of F converging at $R = 0.116$ ($R_w = 0.071$, $w = 1/\sigma^2$), a final shift/error smaller than 0.001 and a residual electron density of $-1.0/+0.9$ eÅ^{-3}. *Zachariasen* parameter $r^* = 1232$. The positions of the H-atoms were calculated and subjected to five cycles of isotropic optimization. Their final refinement was performed in the riding mode. The ClO_4^- anion was severely disordered in that its O-atoms were distributed over a spherical surface enclosing the Cl-atom. Three different orientations could be resolved and were refined assuming equal site-population parameters. Refinement of the structure was further complicated by non-stoichiometric amounts of EtOH in the unit cell. Both the O-atoms of the ClO_4^- anion and the solvent molecule were refined isotropically, while all other structural parameters were optimized anisotropically. Further details of the X-ray structure determinations may be obtained through the *Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH*, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 59211, the authors, and the bibliographical data.

*1,4-Diphenyl-3-(trifluoromethyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**12**). *a*) *N*-Amino-*N*,*N*′-diphenylthiourea [41] (50 g, 206 mmol) was suspended in toluene (500 ml) and the suspension cooled to 0°. Trifluoroacetic anhydride (43.3 g, 206 mmol) was slowly added not allowing the temp. to rise above 10°. The homogeneous mixture was then stirred for further 3 h at 0° and then extracted with 0.5M aq. Na_2CO_3 (350 ml). The org. phase was

separated and dried (Na_2SO_4), and *ca.* 400 ml of toluene were distilled off *in vacuo*. The concentrated toluene soln. was diluted with ligroin (boiling range 35–60°, 100 ml) and the precipitate formed filtered, washed with ligroin, and dried: 39.4 g of *1,4-diphenyl-3-(trifluoromethyl)-1-*H*-1,2,4-triazoline-5-(4*H*)-thione* which was pure enough to use in the next step. M.p. 115–118°. ^{1}H-NMR (250 MHz, (D_6)DMSO): 8.03 (*d*, 2 arom. H); 7.4–7.6 (*m*, 8 arom. H). ^{13}C-NMR (100.6 MHz, (D_6)DMSO): 170.2 (C(5)); 116.8 (*q*, ^1J(C,F) = 272, CF_3); 140.4 (*q*, ^2J(C,F) = 41, C(3)); 129.7, 129.0, 128.2, 124.3 (arom. CH, double intensity); 130.9, 128.9 (arom. CH, single intensity); 137.5, 132.8 (arom. C). ^{19}F-NMR (235.4 MHz, (D_6)DMSO): −63.6. EI- and FAB-MS (pos.): 321 (M^+). Anal. calc. for $C_{15}H_{10}F_3N_3S$ (321.3): C 56.07, H 3.14, F 17.74, N 13.08, S 9.98; found: C 55.9, H 3.3, F 17.6, N 13.1, S 9.9.

b) The thione obtained above (19.3 g, 60 mmol) was suspended in AcOH (45 ml) and 70% perchloric acid (30 ml). H_2O_2 soln. (30%, 42 ml) was then slowly added keeping the temp. below 50°. The mixture was stirred for further 2 h at r.t. and the precipitate filtered, washed with H_2O and recrystallized from abs. EtOH (400 ml): 14.7 g (63%) of **12**. Colorless crystals. M.p. > 200° (dec.). ^{1}H-NMR (400 MHz, (D_6)DMSO): 11.6 (*s*, H–C(5)); 8.03 (*d*, 2 arom. H), 7.75–7.88 (*m*, 8 arom. H). ^{13}C-NMR (100.6 MHz, (D_6)DMSO): 145.7 (C(5)); 143.0 (*q*, ^2J(C,F) = 43, C(3)); 116.1 (*q*, ^1J(C,F) = 273, CF_3); 132.6, 131.6 (arom. CH, single intensity); 130.6, 130.2, 126.3, 121.0 (arom. CH, single intensity); 134.1, 130.3 (C of Ph). EI- and FAB-MS (pos.): 290 (M^+). Anal. calc. for $C_{15}H_{11}ClF_3N_3O_4$ (389.7): C 46.23, H 2.84, Cl 9.10, F 14.62, N 10.78, O 16.42; found: C 45.9, H 2.9, Cl 8.8, F 14.3, N 10.7, O 18.3.

*1,4-Diphenyl-3-methyl-4*H*-1,2,4-triazol-1-ium Perchlorate* (**13**), *1,4-Diphenyl-4*H*-1,2,4-triazol-1-ium Perchlorate* (**14**), *1,4-Diphenyl-3-(4-methoxyphenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**15**), *1,4-Diphenyl-3-(4-chlorophenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**16**), *and 1,4-Diphenyl-3-(4-nitrophenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**17**), were prepared as described in [39].

*1-Phenyl-4-(4-fluorophenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**18**), *1-Phenyl-4-(4-methylphenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**19**), *1-Phenyl-4-(4-nitrophenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**20**), *1-Phenyl-4-(4-methoxyphenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**21**), *1-Phenyl-4-(3-chlorophenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**22**), *and 1-Phenyl-4-(2,6-dimethylphenyl)-4*H*-1,2,4-triazol-1-ium Perchlorate* (**23**), were prepared by reacting 3-phenyl-1,3,4-oxadiazol-3-ium perchlorate [42] with the appropriately substituted aniline as described in [43].

18: Yield 13%. Colorless crystals. M.p. 236–237° (from EtOH). ^{1}H-NMR (400 MHz, (D_6)DMSO): 11.4 (*s*, H–C(5)); 9.95 (*s*, H–C(3)); 8.0 (*m*, 4 arom. H); 7.6–7.8 (*m*, 5 arom. H). ^{13}C-NMR (100.6 MHz, (D_6)DMSO): 162.8 (*d*, ^1J(C,F) = 249, CF); 143.4, 140.6 (C(3), C(5)); 125.4 (*d*, ^3J(C,F) = 9, *C*CCF); 117.2 (*d*, ^2J(C,F) = 24, *C*CF); 130.7 (arom. CH, single intensity); 130.2, 120.7 (arom. CH, double intensity); 134.8, 128.4 (arom. C). ^{19}F-NMR (235.4 MHz, (D_6)DMSO): −109.4. FAB-MS (pos.): 240 (M^+). Anal. calc. for $C_{14}H_{11}ClFN_3O_4$ (339.7): C 49.50, H 3.26, Cl 10.44, F 5.59, N 12.37, O 18.84; found: C 49.2, H 3.3, Cl 10.5, F 5.6, N 12.6, O 18.6.

19: Yield 35%. Colorless crystals. M.p. 247–248° (from MeOH/EtOH). ^{1}H-NMR (400 MHz, (D_6)DMSO); 11.4 (*s*, H–C(5)); 9.98 (*s*, H–C(3)); 8.00 (*d*, 2 arom. H); 7.81 (*d*, 2 arom. H); 7.75 (*t*, 2 arom. H); 7.65 (*t*, 1 arom. H); 7.55 (*d*, 2 arom. H); 2.43 (*s*, Me). ^{13}C-NMR (100.6 MHz, (D_6)DMSO): 143.1 (C(5)); 140.2 (C(3)); 130.6, 130.5, 122.3, 120.8 (arom. CH, double intensity); 130.1 (C_p); 140.7, 134.9, 129.6 (arom. C); 20.6 (Me). FAB-MS (pos.): 236 (M^+). Anal. calc. for $C_{15}H_{14}ClN_3O_4$ (335.7): C 53.66, H 4.20, Cl 10.56, N 12.52, O 19.06; found: C 53.4, H 4.2, Cl 10.6, N 12.5, O 19.2.

20: Yield 19%. Colorless crystals. M.p. 241–242° (from EtOH). ^{1}H-NMR (250 MHz, (D_6)DMSO): 11.7 (*s*, H–C(5)); 10.1 (*s*, H–C(3)); 8.77 (*d*, 2 arom. H); 8.23 (*d*, 2 arom. H); 8.08 (*d*, 2 arom. H); 7.75 (*m*, 3 arom. H). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 143.8 (C(5)); 141.6 (C(3)); 131.6 (C_p, single intensity); 130.9, 126.3, 124.2, 121.2 (arom. CH, double intensity); 148.8, 138.8, 132.0 (arom. C). FAB-MS (pos.): 267 (M^+). Anal. calc. for $C_{14}H_{11}ClN_4O_6$ (366.7): C 45.85, H 3.02, Cl 9.67, N 15.28, O 26.18; found: C 46.0, H 3.1, Cl 9.7, N 15.4, O 26.2.

21: Yield 34%. Colorless crystals. M.p. 252–253° (from EtOH). ^{1}H-NMR (250 MHz, (D_6)DMSO): 11.4 (*s*, H–C(5)); 9.92 (*s*, H–C(3)); 8.02 (*d*, 2 arom. H); 7.85 (*d*, 2 arom. H); 7.72 (*m*, 3 arom. H); 7.30 (*d*, 2 arom. H). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 130.6 (arom. CH, single intensity); 130.2, 124.2, 120.6, 115.2 (arom. CH, double intensity); 143.3 (C(5)); 140.2 (C(3)); 160.6, 134.8, 124.8 (arom. C); 55.8 (MeO). FAB-MS (pos.): 252 (M^+). Anal. calc. for $C_{15}H_{14}ClN_3O_5$ (351.7): C 51.22, H 4.01, Cl 10.08, N 11.95, O 22.74; found: C 51.4, H 4.1, Cl 10.3, N 12.1, O 22.8.

22: Yield 44%. Colorless crystals. M.p. 156–157° (from i-PrOH). ^{1}H-NMR (400 MHz, (D_6)DMSO): 11.5 (*s*, H–C(5)); 10.01 (*s*, H–C(3)); 8.16 (*s*, 1 arom. H); 8.03 (*d*, 2 arom. H); 7.95 (*d*, 1 arom. H); 7.78 (*m*, 4 arom. H); 7.68 (*t*, 1 arom. H). ^{13}C-NMR (100.6 MHz, (D_6)DMSO): 131.9, 130.8, 130.6, 122.7, 121.3 (arom. CH, single intensity); 130.2, 120.7 (arom. CH, double intensity); 143.2 (C(5)); 140.5 (C(3)); 134.7, 134.3, 130.8 (arom. C). FAB-MS (pos.): 256 (M^+). Anal. calc. for $C_{14}H_{11}Cl_2N_3O_4$ (356.2): C 47.21, H 3.11, Cl 19.91 N 11.80, O 17.97; found: C 46.5, H 3.2, Cl 19.3, N 11.6, O 18.6.

23: Yield 72%. Colorless crystals. M.p. 170–172°. ^{1}H-NMR (250 MHz, (D_6)DMSO): 11.2 (*s*, H–C(5)); 9.80 (*s*, H–C(3)); 8.05 (*d*, 2 arom. H of Ph–C(4)); 7.7 (*m*, 3 arom. H of Ph–C(4)); 7.55 (*t*, H_p of Ar–C(1)); 7.41 (*d*, 2 H_m of Ar–C(1)); 2.24 (*s*, 2 Me). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 145.5 (C(5)); 141.9 (C(3)); 130.0, 129.1, 120.8 (arom. CH, double intensity); 131.3, 134.9 (arom. CH, single intensity); 135.0, 134.9, 130.3 (arom. C); 17.3 (Me). FAB-MS (pos.): 250 (M^+). Anal. calc. for $C_{16}H_{16}ClN_3O_4$ (349.8): C 54.94, H 4.61, Cl 10.14, N 12.01, O 18.30; found: C 55.0, H 4.8, Cl 10.3, N 12.1, O 18.4.

2-Phenyl-1,2,4-triazolo[3,4-a]phthalazin-2-ium Tetrafluoroborate (**24**), *2-Phenyl-1,2,4-triazolo[3,4-a]isoquinolin-2-ium Tetrafluoroborate* (**25**), *2-Phenyl-1,2,4-triazolo[4,3-a]pyridin-2-ium Tetrafluoroborate* (**26**), *2-Phenyl-1,2,4-triazolo[4,3-f]phenanthridin-2-ium Tetrafluoroborate* (**27**), *and 2-Phenyl-1,2,4-triazolo[4,3-a]quinolin-2-ium Tetrafluoroborate* (**28**) were prepared as described in [44]. The previously unknown compound **24** was prepared similarly. To *N*-methyl-*N*-nitrosoaniline [45] (7.5 g, 55.1 mmol) in abs. CH_2Cl_2 (20 ml), a suspension of trimethyloxonium tetrafluoroborate (9.0 g, 61.1 mmol) abs. CH_2Cl_2 (50 ml) was slowly added at 0°. After stirring for 3 h at r.t., the soln. was cooled again to 0°, and a soln. of phthalazine (10.0 g, 76.8 mmol) in abs. CH_2Cl_2 (30 ml) was added in one portion, whereby the temp. rose to almost 30°, the color changed from green to red, and a precipitate formed. More abs. CH_2Cl_2 (60 ml) was then added and the suspension stirred overnight at r.t. The precipitate was filtered, washed with CH_2Cl_2 and Et_2O, dried, and recrystallized from H_2O (with addition of activated carbon) to give 6.0 g (33%) of **24**. Colorless crystals. M.p. 255–257°. ^{1}H-NMR (250 MHz, (D_6)DMSO): 12 (*s*, H–C(3)); 9.60 (*s*, 1 arom. H of phthalazine); 8.70 (*d*, 1 arom. H); 8.45 (*d*, 1 arom. H); 8.15–8.30 (*m*, 4 arom. H); 7.7–7.9 (*m*, 3 arom. H). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 142.8 (C(3)); 153.7, 136.0, 134.2, 131.2, 130.4, 123.4 (arom. CH, single intensity); 130.3, 121.1 (arom. CH, double intensity); 138.1, 135.1, 124.1, 119.9 (arom. C). FAB-MS (pos.): 274 (M^+). Anal. calc. for $C_{15}H_{11}BF_4N_4$ (334.1): C 53.93, H 3.32, B 3.24, FF 22.75, N 16.77; found: C 54.0, H 3.4, B 3.1, F 22, N 17.0.

*1,4-Bis(3,5-dichlorophenyl)-3-phenyl-4*H-*1,2,4-triazol-1-ium Perchlorate* (**29**). *a*) To *N*-(3,5-dichlorophenyl)-benzimidoyl chloride [46] (54.4 g, 191 mmol) and Et_3N (50.4 g, 500 mmol) in THF (100 ml), a soln. of (3,5-dichlorophenyl)hydrazine (36.8 g, 208 mmol) in THF (80 ml) was slowly added. After stirring for 2 h at r.t., the solvent was evaporated and the residue dissolved in CH_2Cl_2 (300 ml) and extracted twice with 2% AcOH soln. (100 ml) and twice with H_2O (150 ml). The org. phase was separated, dried (Na_2SO_4), and evaporated at 40°: crude *N-(3,5-dichlorophenyl)benzamide (3,5-dichlorophenyl)hydrazone* (69.05 g, 85%) which was pure enough for the next step.

b) A mixture of Ac_2O (325 ml) and HCOOH (165 ml) was heated for 15 min to 50°. Then crude *N*-(3,5-dichlorophenyl)benzamide (3,5-dichlorophenyl)hydrazone (68 g, 160 mmol; see above) was added. The homogeneous soln. was stirred for 3 h at 60° and then evaporated. The remaining residue was stirred overnight with 50% perchloric acid (340 ml). The precipitate was filtered, washed with H_2O, i-BuOH, and ligroin, and recrystallized twice from MeOH: 54.8 g (64%) of **29**. Colorless crystals. M.p. 245–246°. ^{1}H-NMR (250 MHz, (D_6)DMSO): 11.4 (H–C(5)); 8.25 (*d*, 2 arom. H); 8.12 (*t*, 1 arom. H); 8.08 (*t*, 1 arom. H); 7.83 (*d*, 2 arom. H); 7.58–7.65 (*m*, 5 arom. H). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 144.5 (C(5)); 129.5, 129.3, 125.5, 119.4 (arom. CH, double intensity); 132.8, 131.6, 130.6 (arom. CH, single intensity); 135.8, 135.2 (arom. C, double intensity); 153.2, 136.0, 133.3, 121.3 (arom C, single intensity). EI- and FAB-MS (pos.): 434 (M^+). Anal. calc. for $C_{20}H_{12}N_3O_4Cl_5$ (535.6): C 44.85, H 2.26, Cl 33.10, N 7.85, O 11.95; found: C 45.1, H 2.4, Cl 33.1, N 7.8, O 12.0.

*1,4-Bis(2,6-dimethylphenyl)-3-phenyl-4*H-*1,2,4-triazol-1-ium Perchlorate* (**30**). *a*) To a soln. of (2,6-dimethylphenyl)hydrazinium chloride [47] (17.5 g, 101.4 mmol) and Et_3N (28 g, 276.8 mmol) in THF (100 ml), *N*-(2,6-dimethylphenyl)benzimidoyl chloride [48] (22.5 g, 92.4 mmol) in THF (80 ml) was slowly added. After stirring for 2 h at 50°; the solvent was evaporated and the residue suspended in H_2O and extracted with CH_2Cl_2. The org. phase was dried (Na_2SO_4) and evaporated at 40°: crude *N-(2,6-dimethylphenyl)benzamide (2,6-dimethylphenyl)hydrazone* (34.2 g) which was pure enough to use in the next step.

b) A mixture of Ac_2O (200 ml) and HCOOH (100 ml) was heated for 15 min to 50°. Then the crude *N*-(2,6-dimethylphenyl)benzamide (2,6-dimethylphenyl)hydrazone (34.2 g; see above) was added. The homogeneous soln. was stirred overnight at 100° and then evaporated. The remaining residue was digested for 30 min at r.t. with 30% perchloric acid (80 ml). The precipitate was filtered, washed with H_2O, BuOH, and Et_2O, and recrystallized from EtOH: 27.4 g (65%) of **30**. Colorless crystals. M.p. > 281° (dec.). ^{1}H-NMR (250 MHz, (D_6)DMSO): 10.9 (H–C(5)); 7.2–7.7 (*m*, 10 arom. H); 2.35 (*s*, 2 Me); 2.19 (*s*, 2 Me). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 154.1 (C(5)); 130.0, 129.9, 129.6, 128.6 (arom. CH, double intensity); 133.4, 132.4, 132.3 (arom. CH, single intensity); 135.6, 135.5 (arom. C, double intensity); 147.7, 133.8, 130.6, 122.5 (arom. C, single intensity); 17.7, 17.4 (Me). EI- and FAB-MS (pos.): 354 (M^+). Anal. calc. for $C_{24}H_{24}ClN_3O_4$ (453.9): C 63.50, H 5.33, Cl 7.81, N 9.26, O 14.10; found: C 63.2, H 5.6, Cl 7.9, N 9.2, O 14.1.

*4,5-Dihydro-5-methoxy-1,3,4-triphenyl-1*H-*1,2,4-triazole* (**31**), *4,5-dihydro-5-methoxy-3-(4-methoxyphenyl)-1,4-diphenyl-1*H-*1,2,4-triazole* (**32**), *3-(4-chlorophenyl)-4,5-dihydro-5-methoxy-1,4-diphenyl-1*H-*1,2,4-triazole* (**33**), *4,5-dihydro-5-methoxy-3-(4-nitrophenyl)-1,4-diphenyl-1*H-*1,2,4-triazole* (**34**), *and 1,4-bis(3,5-dichlorophenyl)-4,5-dihydro-5-methoxy-3-phenyl-1*H-*1,2,4-triazole* (**35**) were prepared according to the following general method: To a soln. or suspension of 1,3,4-triaryl-4*H*-1,2,4-triazol-1-ium perchlorate (25 mmol) in MeOH (150 ml), a soln. of NaOMe (1.4 g, 26 mmol) in MeOH (30 ml) was added at r.t. under N_2. After stirring for 10 min, the MeOH was evaporated at r.t. The residue was stirred with Et_2O and the insoluble $NaClO_4$ removed by filtration. The residue remaining after evaporation of the Et_2O was recrystallized from MeOH to give the desired product.

31: Yield 63%. The physical data were reported in [15].

32: Yield 62%. M.p. > 97° (dec.). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.5 (*d*, 2 arom. H); 7.2–7.35 (*m*, 7 arom. H); 7.13 (*m*, 2 arom. H); 6.9 (*m*, 1 arom. H); 6.85 (*d*, 2 arom. H); 6.73 (*s*, H–C(5)); 3.8 (*s*, *Me*OC$_6$H$_4$); 3.2 (*s*, MeO–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 160.5 (MeO–*C*(arom.)); 145.6 (C(3)); 129.1, 129.0, 128.9, 123.1, 114.0, 112.8 (arom. CH, double intensity); 125.2, 120.0 (arom. CH, single intensity); 101.0 (C(5)); 142.2, 140.2, 120.1 (arom. C); 55.3 (*Me*OC$_6$H$_4$); 47.1 (*Me*O–C(5)). EI-, CI-, and FAB-MS (pos.): 327 [*M* – MeOH]$^+$). Anal. calc. for $C_{22}H_{21}N_3O_2$ (359.4): C 73.52, H 5.89, N 11.69, O 8.90; found: C 73.9, H 5.4, N 11.9, O 8.8.

33: Yield 64%. M.p. > 97° (dec.). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.5 (*d*, 2 arom. H); 7.2–7.4 (*m*, 8 arom. H); 7.17 (*t*, 1 arom. H); 7.07 (*d*, 2 arom. H); 6.95 (*m*, 1 arom. H); 6.75 (*s*, H–C(5)); 3.20 (*s*, MeO–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 129.2, 129.1, 128.8, 128.7, 123.2, 112.9 (arom. CH, double intensity); 125.5, 120.4 (arom. CH, single intensity); 101.1 (C(5)); 135.2 (ClC); 144.6 (C(3)); 142.0, 139.9, 126.3 (arom. C); 47.1 (*Me*O–C(5)). EI-, CI-, and FAB-MS (pos.): 331 ([*M* – MeOH]$^+$). Anal. calc. for $C_{21}H_{18}ClN_3O$ (363.89): C 69.32, H 4.99, Cl 9.74, N 11.55, O 4.40; found: C 69.0, H 5.1, Cl 9.8, N 11.5, O 4.9.

34: Yield 86%. M.p. > 103° (dec.). ^{1}H-NMR (250 MHz, $CDCl_3$): 8.18 (*d*, 2 arom. H); 7.75 (*d*, 2 arom. H); 7.2–7.4 (*m*, 7 arom. H); 7.08 (*d*, 2 arom. H); 6.97 (*m*, 1 arom. H); 6.80 (*s*, H–C(5)); 3.20 (*s*, MeO–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 129.4, 129.3, 127.8, 123.8, 123.3, 113.2 (arom. CH, double intensity); 126.0, 121,1 (arom. CH, single intensity); 101.4 (C(5)); 147.7 (CNO_2); 143.4 (C(3)); 141.4, 139.7, 133.9 (arom. C); 47.2 (*Me*O–C(5)). EI- and FAB-MS (pos.): 374 (M^+). Anal. calc. for $C_{21}H_{18}N_4O_3$ (374.4): C 67.37, H 4.85, N 124.96, O 12.82; found: C 67.2, H 4.8, N 15.2, O 12.8.

35: Yield 72%. M.p. 149–150° (dec.). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.55 (*m*, 2 arom. H); 7.4 (*m*, 3 arom. H); 7.20 (*d*, 2 arom. H); 7.04 (*t*, 1 arom. H); 6.97 (*d*, 2 arom. H); 6.91 (*t*, 1 arom. H); 6.68 (*s*, H–C(5)); 3.18 (*s*, MeO–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 128.9, 127.5, 120.7, 111.4 (arom. CH, double intensity); 130.4, 125.4, 120.3 (arom. CH, single intensity); 99.8 (C(5)); 135.6, 135.3 (CCl); 143.0 (C(3)); 145.6, 141.3, 126.4 (arom. C); 47.5 (*Me*O–C(5)). EI- and FAB-MS (pos.): 435 ([*M* – MeOH]$^+$). Anal. calc. for $C_{21}H_{15}Cl_4N_3O_3$ (467.2): C 53.99, H 3.24, Cl 30.35, N 8.99, O 3.42; found: C 54.2, H 3.5, Cl 29.8, N 9.0, O 3.4.

*2,3-Dihydro-2-methoxy-1,3-diphenyl-1*H-*benzimidazole* (**36**). To a soln. of NaOMe (0.27 g, 5.0 mmol) in degassed MeOH (15 ml), solid 1,3-diphenyl-1*H*-benzimidazol-3-ium iodide (**10**) [37] (2.0 g, 5.0 mmol) was added under N_2. The mixture was stirred for 1 h at 40° under N_2 whereby a precipitate was formed. This precipitate was filtered and recrystallized from MeOH: 1.0 g (66%) of **36**. Colorless crystals which turn red on exposure to air. M.p. 97–98°. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.55 (*d*, 4 arom. H); 7.36 (*t*, 4 arom. H); 7.15 (*m*, 2 arom. H); 7.08 (*m*, 2 arom. H); 6.85 (*m*, 2 arom. H); 6.65 (*s*, H–C(2)); 3.10 (*s*, MeO). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 129.4, 119.1 (arom. CH, quadruple intensity); 123.4, 119.7, 108.6 (arom. CH, double intensity); 141.1, 134.7 (arom. C); 102.2 (C(2)); 46.8 (MeO). EI- and FAB-MS (pos.): 302 (M^+). Anal. calc. for $C_{20}H_{18}N_2O$ (302.4): C 79.44, H 6.00, N 9.26, O 5.29; found: C 79.3, H 6.0, N 9.4, O 5.2.

*1,3,4-Triphenyl-4*H-*1,2,4-triazol-1-ium-5-ide* (**37**) was prepared as described previously [15]. UV/VIS (THF): 340 (10800), 289 (8200), 236 (21800).

*5-(Hydroxymethyl)-1,3,4-triphenyl-4*H-*1,2,4-triazol-1-ium Perchlorate* (**38**). Paraformaldehyde (5.0 g, 167 mmol), 1,3,4-triphenyl-4*H*-1,2,4-triazolium perchlorate (**11**; 5.0 g, 12.6 mmol) and K_2CO_3 (5 mg, 0.036 mmol) were suspended in THF (130 ml) and i-PrOH (0.5 ml) and heated to reflux under N_2 for 6 h. If the mixture became clear before the end of this period, more paraformaldehyde was added. Excess paraformaldehyde must be present at the end of the reaction. Upon cooling, the unreacted paraformaldehyde and **11** were filtered off. The clear filtrate was dried (Na_2SO_4) and evaporated at r.t. The residue was then stirred with 10% perchloric acid (50 ml) for 15 min at r.t. The remaining solid was collected by filtration, washed with H_2O, dried *in vacuo* at r.t., and quickly recrystallized from EtOH: 3.5 g (65%) of **38**. Colorless crystals. M.p. 182–183°. ^{1}H-NMR (250 MHz, (D_6)DMSO): 7.95 (*m*, 2 arom. H); 7.80 (*m*, 3 arom. H); 7.70 (*m*, 5 arom. H); 7.60 (*m*, 1 arom. H); 7.50 (*m*, 4 arom. H); 6.38 (*t*, OH); 6.67 (*d*, CH_2O). ^{13}C-NMR (62.9 MHz, (D_6)DMSO): 131.6, 131.4, 131.1 (arom. CH, single intensity); 130.2, 130.0, 129.2, 129.0, 127.6, 125.0 (arom, CH, double intensity); 153.1, 152.8, (C(3), C(5)); 134.7,

132.0, 122.5 (arom. C); 52.0 (CH_2). EI- and FAB-MS (pos.): 328 (M^+). Anal. calc. for $C_{21}H_{18}ClN_3O_5$ (427.8): C 58.95, H 4.24, Cl 8.29, N 9.82, O 18.70; found: C 58.6, H 4.3, Cl 8.2, N 9.8, O 18.7.

*5-(1-Hydroxypropyl)-1,3,4-triphenyl-4*H-*1,2,4-triazolium Perchlorate* (**42**). Propionaldehyde (36.6 g, 630 mmol), **11** (5.0 g, 12.6 mmol), and K_2CO_3 (5 mg, 0.036 mmol) were suspended in THF (180 ml) and heated to reflux under N_2 for 6 h whereby the mixture became clear. The solvents were then removed *in vacuo* at r.t., and the residue was stirred with 10% perchloric acid (50 ml) for 15 min at r.t. The remaining solid was collected by filtration, washed with H_2O and dried *in vacuo* at r.t.: 4.97 g (87%) of **42**. Colorless microcrystalline powder. Attempts to recrystallize the product from EtOH led only to decomposition into propionaldehyde and **11**. **42**: M.p. > 180° (dec.). ^{1}H-NMR (400 MHz, (D$_6$)DMSO): 7.43–748 (*m*, 15 arom. H); 6.53 (*d*, ^3J(H,H) = 5 OH); 4.67 (*m*, MeCH_2CH); 1.74 (*m*, 1 H, MeCH_2CH); 1.44 (*m*, 1 H, MeCH_2CH); 0.76 (*t*, ^3J(H,H) = 7, *Me*CH$_2$CH). ^{13}C-NMR (100.6 MHz, (D$_6$)DMSO): 131.96, 131.76, 131.66 (arom. CH, single intesity); 130.0, 129.85, 129.3, 129.3, 128.9, 126.3 (arom. CH, double intensity); 154.7, 153.3 (C(3), C(5)); 135.1, 131.3, 122.6 (arom. C); 65.9 (MeCH$_2$*C*H); 26.8 (MeCH$_2$CH); 10.0 (*Me*CH$_2$CH): ESI (pos. and neg.): 356 (M^+). Anal. calc. for $C_{23}H_{22}ClN_3O_5$ (455.9): C 60.60, H 4.86 Cl 7.78, N 9.22, O 17.55; found C 60.7, H 5.0, Cl 7.8, N 9.2, O 17.2.

Computational Details. All geometry optimizations were done at the *ab initio* SCF level using the parallel version of the program TURBOMOLE [49] and using split-valence basis sets [50] (for C, N, and O, 7s4p contracted to 3s2p according to the scheme {511/31}; for S, 10s7p contracted to 4s3p according to the scheme {5311/511}; for H, 4s contracted to 2s according to the scheme {31}). For C, N, and O a set of d-polarization functions was added with exponents 0.8 (C), 1.0 (N), 1.2 (O), and 0.55 (S). The geometry optimization was terminated when |gradient| < 0.5 kJ/mol/Å. The energies were calculated at the MP2 level [51] using the SCF geometry and a triple-zeta basis set (for C, N, and O, 11s6p contracted to 5s3p according to the scheme {61211/411}; for S, 12s9p contracted to 7s5p according to the scheme {5121111/51111}; for H, 5s contracted to 3s according to the scheme {311}). For C, N, O, and S, a set of d-polarization functions with exponents 0.8 (C), 1.0 (N), 1.2 (O); and 0.55 (S) and for H, a p-function with exponent 0.8 were added.

The vibrational frequencies needed to compute the thermodynamic parameters (ΔG and ΔH) were computed from the second derivatives of the energy on SCF level with respect to the coordinates using the first basis set. The thermodynamic data were calculated as described in [52].

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