Molecules **1996**, *1*, 264 - 270

The Vilsmeier Polyformylation Reaction of Phenylacetone. Synthesis of New Pyridines, Naphthyridines and Benzodiazepines

Manfred Weissenfels[1], Manfred Pulst[1], Wei Cao[1], Dirk Riedel[1], Dieter Greif[2,*]

[1] Institut für Organische Chemie, Fakultät für Chemie und Mineralogie der Universität Leipzig, Talstraße 35, D-04103 Leipzig, Germany

[2] Fachbereich Mathematik/Naturwissenschaften der Hochschule für Technik, Wirtschaft und Sozialwesen Zittau/ Görlitz (FH), Theodor-Körner-Allee 16, D-02763 Zittau, Germany; Tel.: +49-3583-611706 (greif@na-wiss.htw-zittau.de)

Received: 29 October 1996 / Accepted: 18 December 1996 / Published: 12 March 1997

Abstract

New polyformylation derivatives of phenylacetone and *m*-trifluoromethylphenylacetone from the reaction with the Vilsmeier reagent are described as well as their amazing reactions with water, methanol and several primary amines. In few steps new substituted pyridines, naphthyridines and benzodiazepines are available in good yields.

Keywords: Vilsmeier reaction, polyformylated derivatives of phenylacetone and *m*-trifluoromethylacetophenone, iminium salts, pyridinium salts, naphthyridinium salts, benzodiazepinium salts

Introduction

Several carbonyl compounds with methyl and methylene groups adjacent to the C=O group are converted to polyformylated derivatives using an excess of the Vilsmeier reagent. In the field of ketones for example, acetone and homologous simple aliphatic ketones [1], cyclopentanone and cyclohexanone [2] are described as well as acetylacetone [3] and several comparable dicarbonyl moieties [4]. Likewise unsaturated aliphatic ketones give rise to polyformylated derivatives, often together with a spontaneous formation of arenes by assuming a 6 π electrocyclic ring closure reaction [3–5]. One pot reactions to heterocycles are reported starting from dibenzyl ketone [6] and phenylacetone [7]. Furthermore bis and tris formylation derivatives can be received, beside the monochloroformylation reaction products, from various heterocyclic carbonyl compounds and also from simple amides. These results are included in the review article by C. M. Marson [8] and are of great interest for organic synthesis.

Our early interest to phenylacetone was given by the convenient monochloroformylation reaction yielding 3-chloro-2-phenyl-2-butenal [9]. Repeating this reaction several times confirmed the regioselective attack of the

* *To whom correspondence should be addressed*

† *Presented at the Joint 12th Symposium on the Chemistry of Heterocyclic Compounds (SCHHC) and the 6th Blue Danube Symposium on Heterocyclic Chemistry (BDSHC), Brno, Czech Republic, September 1–4, 1996.*

Vilsmeier reagent exclusively to the -CH_2- group. After using this β-chlorovinylaldehyde as C-3 building block for synthesis of heterocycles [10], we now can report about definite polyformylation results including the methyl group of phenylacetone and *m*-trifluoromethylphenylacetone [11].

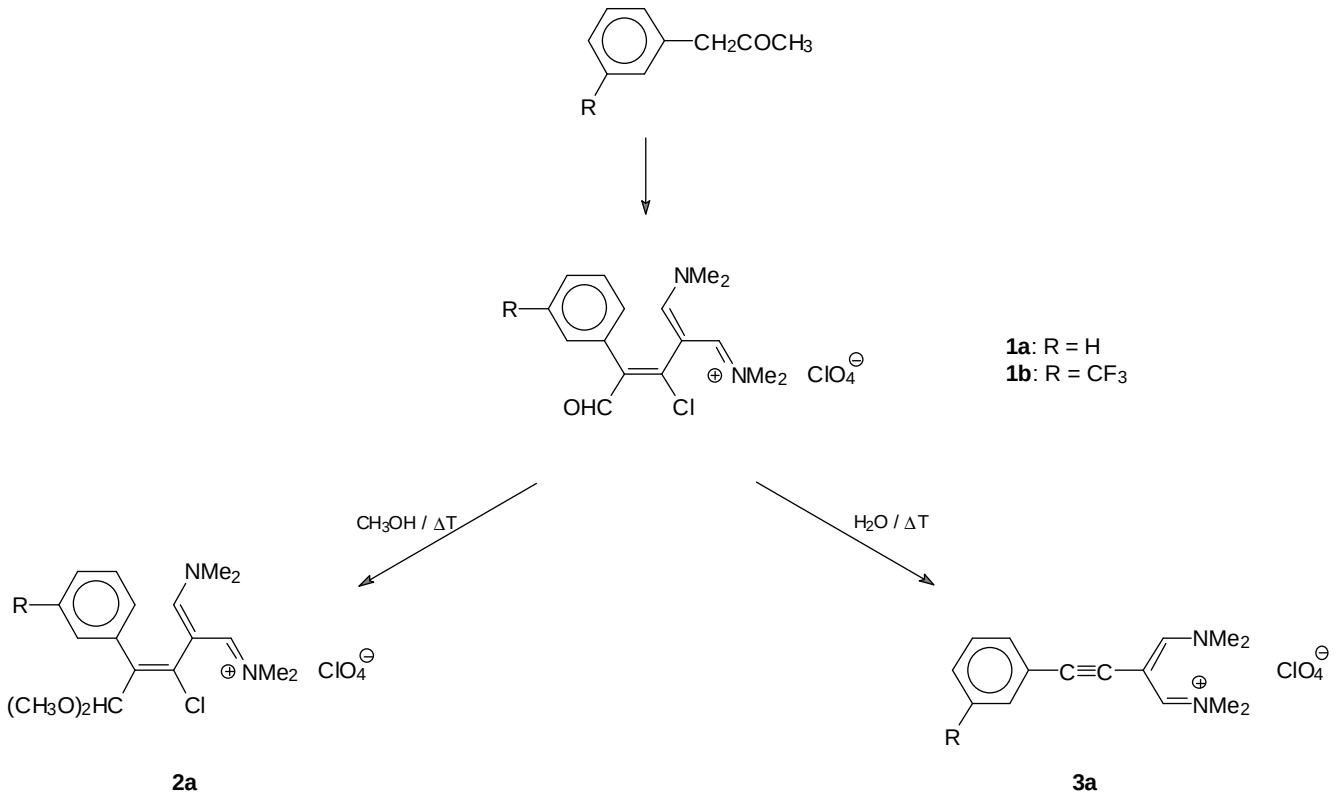
Results and Discussion

Phenylacetone and *m*-trifluoromethylphenylacetone react with a five times excess of the Vilsmeier reagent at a temperature of 70 °C for two hours to give **1a-b**, available as perchlorates after addition of 70% perchloric acid to the reaction mixture. Recrystallization from acetonitrile gives the pure salts, refluxing the crude product **1a** with methanol causes the formation of the dimethylacetale **2a**. Structural elucidation and further reactions confirmed the postulated formulae in Scheme 1.

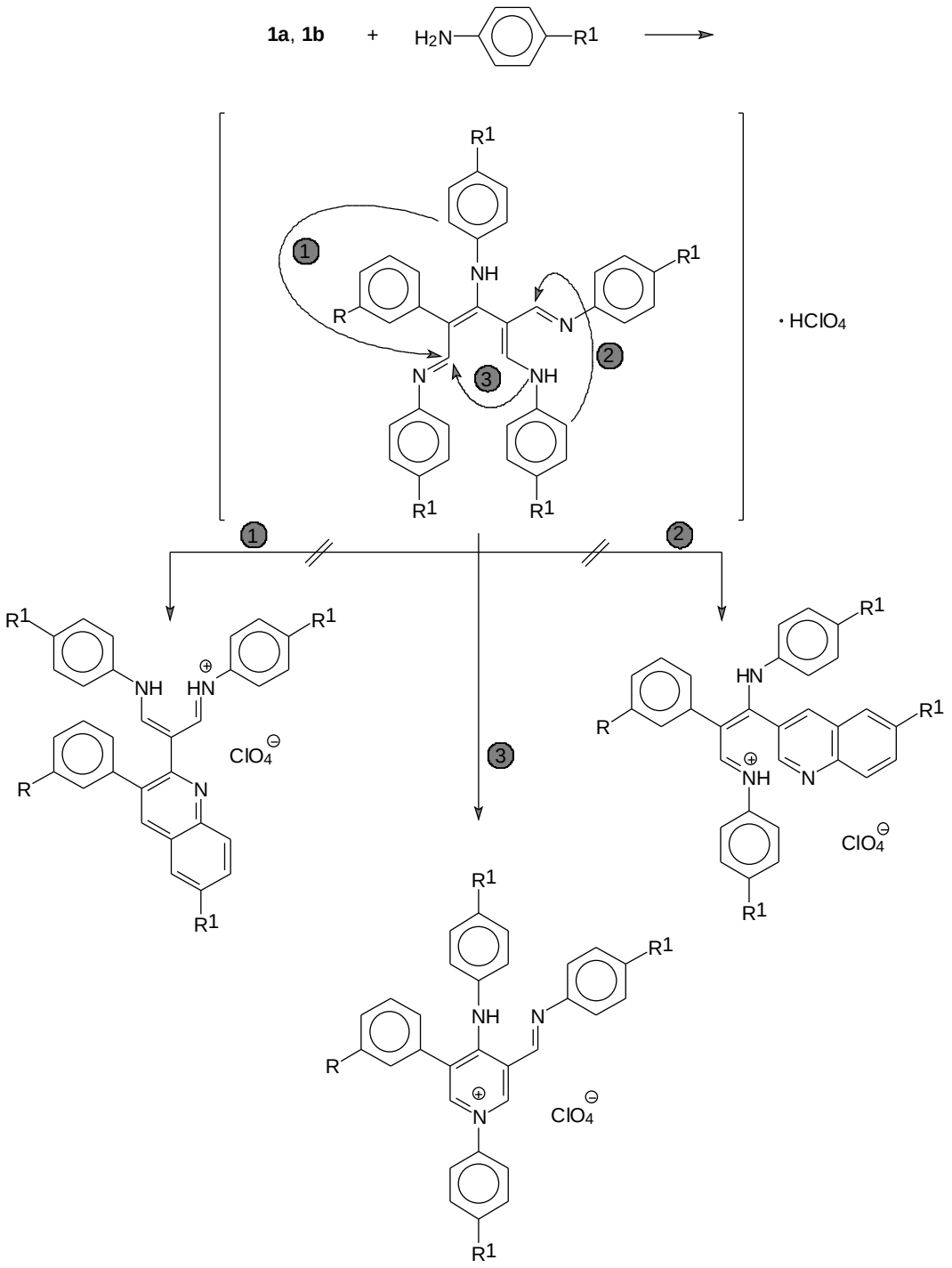
Attempts to hydrolize **1a-b** have been successful in the case of **1a** by warming the crude compound with water to give the symmetrical resonance stabilized cation **3a**, available as perchlorate (Scheme 1). This result is in contrast to investigations by Arnold, Zemlicka, Bodendorf and Mayer [2a, 12], who needed basic reaction conditions for the fragmentation of the β-chlorovinylaldehyde structure yielding an acetylenic bond. Doubtless the reason for the decomposition of **1a** under mild conditions is the above mentioned resonance stability of **3a**. It is not clear why these reactions failed with **1b**.

^{1}H-NMR investigations of **1a, 1b** and **3a** indicated the equality of six protons in two methyl groups and of another six protons in two opposite methyl groups with another sterical direction in the magnetic field (**1a***, **1b**** and **3a***). The reason for this effect may be the partial double bond character of C-N bonds and consequently the restricted rotation around this bonds at room temperature. Raising the temperature during NMR studies allowed one to find out the coalescence temperature for **1a** at 104 °C, **1b** at 93 °C and **3a** at about 165 °C (by abstracting calculation after measurements up to 150 °C).

Attempts to receive **1a** respectively **1b** starting from destilled 3-chloro-2-phenyl-2-butenal or the analogous CF_3-substituted compound failed under the conditions of the Vilsmeier polyformylation. These results are understandable because it is not correct to compare the reaction mechanism of unsaturated aldehydes and iminium salts, the primary reaction products during the Vilsmeier reaction. So we assume that it is possible, on the one hand, to produce the iminium salt of the monochloroformylation step under the well known conditions and to hydrolyze this product to receive the free aldehyde or, on the other hand,

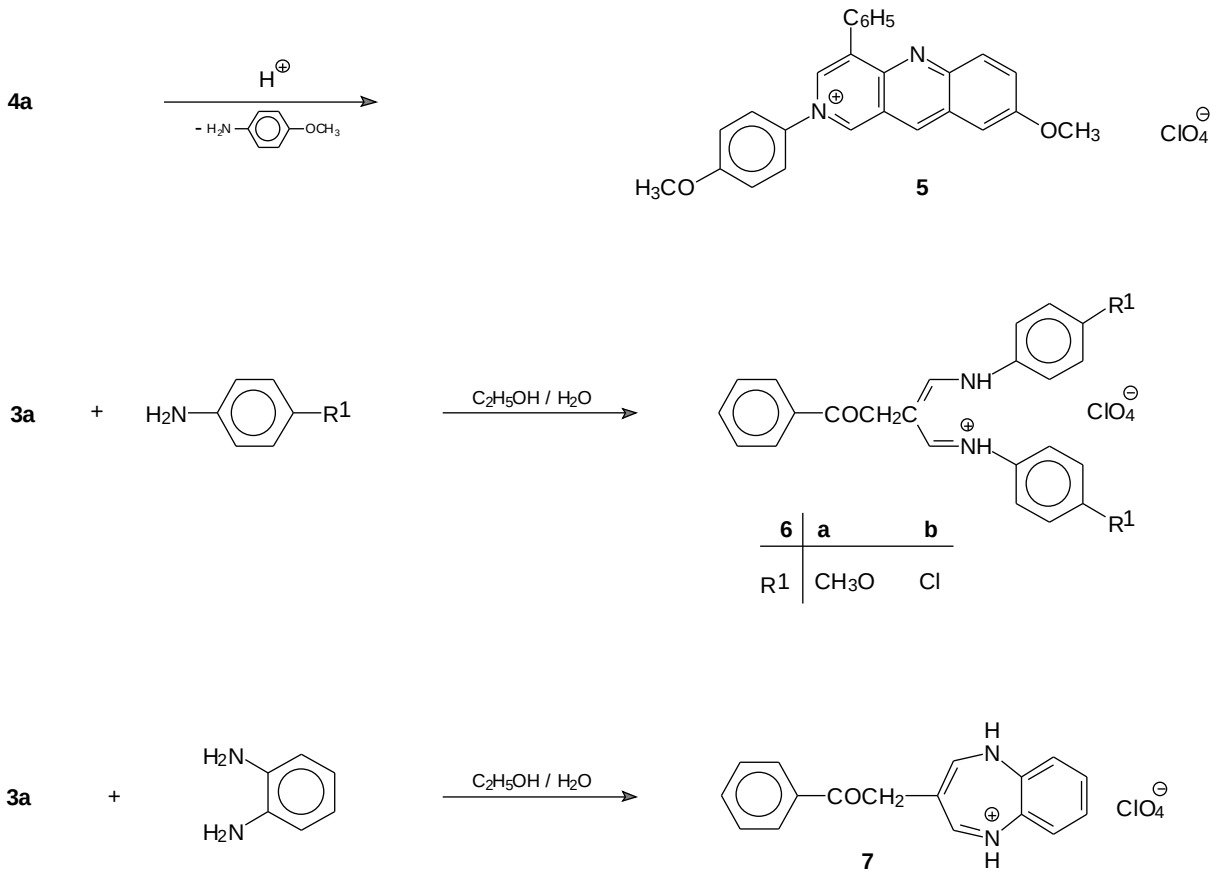


Scheme 1



4	**a**	**b**	**c**	**d**	**e**
R^1	CH_3O	CH_3	Cl	CH_3O	NH_2
R	H	H	H	CF_3	CF_3

Scheme 2



Scheme 3

to continue the Vilsmeier reaction with a large excess of the reagent to get isolable tris-formylated derivatives **1a** and **1b** including the double attack of the reagent to the methyl group of the starting ketone.

1a, b and **3a** may be considered as special substituted malonic dialdehyde derivatives with a convenient stability as perchlorates and a good reactivity to several nucleophiles. So, investigations of reactions with several substituted anilines**** gave the following results:

1a, b reacts with *p*-toluidine, *p*-anisidine and *p*-chloroaniline to give pyridinium salts **4a-e** (Scheme 2). We assume as a first reaction product the postulated intermediate in Scheme 2, generated by the reaction of all electrophilic carbon atoms of **1** with the nucleophiles and therefore a four times excess of anilines has been used.

* δ (ppm) = 3.30 (s, 6H, NMe_2); 3.37 (s, 6H, NMe_2); $\Delta G^{\#}$ = 79.6 kJ mol^{-1} (free rotation)

** δ (ppm) = 3.37 (s, 6H, NMe_2); 3.44 (s, 6H, NMe_2); $\Delta G^{\#}$ = 80.0 kJ mol^{-1} (free rotation)

*** δ (ppm) = 3.43 (s, 6H, NMe_2); 3.67 (s, 6H, NMe_2); $\Delta G^{\#}$ = 85.2 kJ mol^{-1} (free rotation)

**** Using aniline as parent compound no definite results were available

Possible alternative ring closure reactions to give quinoline derivatives are also demonstrated in scheme 2. But the reaction via pathways 1 and 2 could be excluded by means of H-H COSY NMR spectra, which indicate three identical *p*-substituted benzene nuclei in the molecular structure.

Attempts with other molar ratios of the starting materials gave no change in the results, but the yields were, as expectied, very low. Furthermore, conceivable ring closure reactions have been realized, starting from **4a**, for example, to give a 1,6-naphthyridinium perchlorate **5** (Scheme 3).

p-Anisidine and *p*-chloroaniline reacted with **3a** to give **6a,b** (Scheme 3) by substitution of the dimethylamino groups; *o*-phenylenediamine gave rise to the benzodiazepinium salt **7**. Remarkable for these results was the constraining regioselective hydratation of the triple bond during this reaction in the presence of traces of water (96% ethanol as solvent) yielding the phenacyl derivatives.

In summary, our results indicate that an enlargement of the limited pool of wellknown polyformylated derivatives via the Vilsmeier reaction is indeed possible. It seems important to us to look for an optimal, preferably low reaction temperature (65–70 °C in this paper) and to investigate carefully the isolation procedure of the iminium perchlorates from the ice-water diluted reaction mixture.

Further amazing reactions of new iminium salts are to be expected.

Experimental

Melting points were measured with a Boetius apparatus and are corrected. Infrared spectra were recorded as potassium bromide pellets with a spectrophotometer UR 20 (Carl Zeiss Jena) and ultraviolet spectra were taken on a spectral photometer Specord (Carl Zeiss Jena). ^{1}H-NMR spectra were obtained on a Tesla BS 487 C spectrometer (at 80 MHz), on a Varian Gemini spectrometer (at 200 MHz) or on a Varian Unity spectrometer (at 400 MHz) and are reported in ppm on the δ scale. The internal standard is the solvent used. Mass spectra were performed by direct ionization (EI at 70 eV) on a Varian Mat CH6 apparatus or by the FAB method on a ZAP-HSQ from VG Analytical. Elemental analyses were taken from an automatic analyzer CHN-O Rapid Heraeus.

3-Chloro-4-formyl-2-dimethylaminomethylene-4-phenyl-3-buten-1-ylidene-dimethyliminium Perchlorate ***1a***

The Vilsmeier reagent was prepared from 46 ml (0.5 mol) $POCl_3$ and 47 ml (0.6 mol) DMF at –5 °C dropping the $POCl_3$ into the cooled and stirred DMF in a three necked flask. After addition was completed, the mixture was allowed to warm to +5 °C. Then 13.5 ml (0.1 mol) phenylacetone were added dropwise with continued stirring and cooling. Afterwards the mixture was heated to 70 °C for two hours. A correct control of the temperature (80 °C maximum) is important. The mixture was allowed to cool to room temperature and to stand overnight. Then the mixture was poured onto crushed ice and water (2:1) and 75 ml of 70% perchloric acid was added slowly, with 40 °C as the maximum temperature. The mixture was allowed to stand overnight for crystallization of the viscous oil. The crystals were filtered and recrystallized from acetonitrile to yield 29.8 g (76%) of colorless needles. m.p. 206 °C; IR (KBr), ν(cm^{-1}):1610, 1660, 1680; UV(λ_{max}, nm) (lgε):304 (4.53); ^{1}H-NMR ($CDCl_3$, 80 MHz), δ(ppm): 9.85 (s, 1H, CHO), 7.85 (s, 2H 2 CH = N), 7.18–7.47 (m, 5H, C_6H_5), 3.38 (s, 6H, 2×CH_3), 3.30 (s, 6H, 2×CH_3); MS: m/z = 263 (M^+-$HClO_4$-CHO), 248 (M^+-$HClO_4$-NMe_2); MS (FAB): m/z = 291 (M^+-$HClO_4$).

$C_{16}H_{20}Cl_2N_2O_5$ (391.30) Calcd.: C 49.26, H 5.14, Cl 18.07, N 7.14. Found: C 49.11, H 5.10, Cl 18.34, N 7.19.

3-Chloro-4-(3-triflourmethylphenyl)-4-formyl-2-dimethylaminomethylene-3-buten-1-ylidene-dimethyliminium Perchlorate ***1b***

The Vilsmeier reagent was prepared as described for **1a**. 20 g (0.1 mol) *m*-trifluoromethyl-phenylacetone were added dropwise at about 10 °C. The mixture was heated to 65 °C for two hours, allowed to cool to room temperature and poured into a mixture of crushed ice and water. After this 75 ml of 70% perchloric acid were added slowly. The mixture was allowed to stand overnight for crystallization of the viscous oil. The crystals were filtered, washed with cold water and dried. Then the crystals were dissolved in a small amount of acetonitrile and a layer of ether was added to yield 35.8 g (78%) of light yellow crystals. m.p. 183 °C; IR (KBr) , ν(cm^{-1}):1090, 1160, 1200, 1600, 1680; ^{1}H-NMR (DMSO-D_6, 200 MHz), δ(ppm): 9.84 (s, 1H, CHO), 7.62–7.96 (m, 4H, C_6H_4) 3.44 (s, 6H, 2×CH_3), 3.37 (s, 6H, 2×CH_3); MS(FAB) (%): m/z = 361 (35) (M^+-$HClO_4$, ^{37}Cl), 359 (100) (M^+-$HClO_4$), ^{35}Cl).

$C_{17}H_{19}Cl_2F_3N_2O_5$ (459.22) Calcd.: C 44.46, H 4.17, N 6.10. Found: C 44.86, H 4.70, N 6.60.

3-Chloro-5,5-dimethoxy-2-dimethylaminomethylene-4-phenyl-3-penten-1-ylidene-dimethyliminium Perchlorate ***2a***

The crude product from procedure **1a** was crystallized from methanol instead of acetonitrile to yield 34.1 g (78%) of colorless needles. m.p.154 °C (decomp.); IR (KBr), ν(cm^{-1}): 1100, 1280, 1600; ^{1}H-NMR ($CDCl_3$, 80 MHz), δ(ppm): 9.96 (s. 1H, O-CH-O), 7.81 (s, 2H, 2×CH), 7.27–7.48 (m, 5H, C_6H_5), 3.47 (s, 6H, 2×CH_3), 3.46 (s, 6H, 2×CH_3), 3.40 (s, 6H, 2×OCH_3); MS: (FAB): m/z = 337 (M^+-$HClO_4$).

$C_{18}H_{26}Cl_2N_2O_6$ (437.30) Calcd.: C 49.47, H 5.99, Cl 16.22, N 6.41. Found: C 49.32, H 5.75, Cl 15.88, N 6.40.

2-Dimethylaminomethylene-4-phenyl-3-butin-1-ylidene-dimethyliminium Perchlorate ***3a***

39 g **1a** (0.1 mol) were treated with 50 ml of water. The stirred mixture was heated to 80 °C for about two hours until the color had changed from yellow to colorless. After cooling to room temperature the crystals obtained were filtered, washed with cold water and dried in the air. Recrystallization from methanol yielded 18.9 g (58%) of colorless crystals. m.p. 223 °C; IR (KBr), ν(cm^{-1}): 1620, 1670, 2220; ^{1}H-NMR ($CDCl_3$, 80 MHz), δ(ppm): 7.97 (s, 2H, 2× = C*H*-) 7.35 (m, 5H, C_6H_5), 3.67 (s, 6H, 2×CH_3), 3.43 (s, 6H, 2×CH_3); MS: m/z = 227 (M^+-$HClO_4$), 170 (M^+-$HClO_4$-$CHNMe_2$).

$C_{15}H_{19}ClN_2O_4$ (326.78) Calcd.: C 55.15, H 5.86, Cl 10.85, N 8.57. Found: C 54.81, H 5.81, Cl 11.91, N 8.61.

General Procedure for the Preparation of Pyridinium Salts

0.01 mol **1a** resp. **1b** were dissolved in 120 ml boiling ethanol followed by the addition of a solution of 0.04 mol of the corresponding substituted amine in 20 ml ethanol. The reaction mixture was refluxed for some minutes and al-

lowed to cool to room temperature. After storing the mixture overnight the crystals which precipitated were filtered and recrystallized from methanol.

1-(4-Methoxyphenyl)-4-(4-methoxyphenyl-amino)-3-(4-methoxyphenyl-iminomethylene)-5-phenyl-pyridinium Perchlorate ***4a***

3.9 g **1a** and 5.0 g *p*-anisidine gave 2.3 g (38%) yellow needles. m.p. 165 °C (decomp.); IR (KBr), ν(cm^{-1}): 1100, 1250, 1510. 1640; ^{1}H-NMR ($CDCl_3$, 400 MHz), δ(ppm): 14.010 (s, 1H, NH), 9.110 (s, 1H, CH, pyridine nucl.), 8.972 (s, 1H, pyridine nucl.), 7.800 (s, 1H, CH=N), 7.078–7.118 (m, 5H, C_6H_5), 7.639–7.661 (d, 4H, C_6H_4), 6.983–7.005 (d, 4H, C_6H_4), 7.340–7.362 (d, 4H, C_6H_4), 6.777–6.794 (d, 4H, C_6H_4), 6.799–6.816 (d, 4H, C_6H_4), 6.502–6.524 (d, 4H, C_6H_4) 3.181 (s, 3H, OCH_3), 3.727 (s, 3H, OCH_3), 3.680 (s, 3H, OCH_3); MS: (FAB): m/z = 516 (M^+-$HClO_4$).

$C_{33}H_{30}ClN_3O_7$ (616.03) Calcd.: C 64.34, H 4.91, Cl 5.75, N 6.82. Found: C 64.34, H 4.75, Cl 6.21, N 6.62.

1-(4-Methylphenyl)-4-(4-methylphenyl-amino)-3-(4-methylphenyl-iminomethylene)-5-phenyl-pyridinium Perchlorate ***4b***

1.6 g **1a** and 1.8 g *p*-toluidine gave 0.6 g (26%) yellow crystals. m.p. 161 °C (decomp.); IR (KBr), ν(cm^{-1}): 1100, 1640; ^{1}H-NMR ($CDCl_3$, 80 MHz), δ(ppm): 14.034 (s, 1H, NH), 9.129 (s, 1H, CH, pyridine nucl.), 9.009 (s, 1H, CH, pyridine nucl.), 7.849 (s, 1H, CH = N), 6.753–7.678 (m, 17 H, aromat.), 2.302 (s, 6H, 2×CH_3), 2.172 (s, 3H, CH_3).

$C_{33}H_{30}ClN_3O_4$ (568.04) Calcd.: C 69.77, H 5.32, Cl 6.24, N 7.40. Found: C 69.58, H 4.99, Cl 7.02, N 7.47.

1-(4-Chlorophenyl)-4-(4-chlorophenyl-amino)-3-(4-chlorophenyl-iminomethylene)-5-phenyl-pyridinium Perchlorate ***4c***

3.9 g **1a** and 5.1 g *p*-chloroaniline gave 2.4 g (38%) yellow needles from methanol/acetonitrile (3:1). m.p. 214 °C; IR (KBr), ν(cm^{-1}): 1100, 1510, 1640; ^{1}H-NMR ($CDCl_3$, 400 MHz), δ(ppm): 13.261 (s, 1H, NH), 9.387 (s, 1H, CH, pyridine nucl.), 9.213 (s, 1H, CH pyridine nucl.), 8.821 (s, 1H, CH = N), 8.050–8.072 (d, 4H, C_6H_4), 7.917–7.939 (d, 4H, C_6H_4), 7.699–7.721 (d, 4H, C_6H_4), 7.621–7.642 (d, 4H, C_6H_4), 7.260–7.367 (m, 5H, C_6H_5), 7.159–5.181 (d, 4H, C_6H_4), 7.092–7.114 (d, 4H, C_6H_4); MS: (FAB): m/z = 528 (M^+ - $HClO_4$).

$C_{30}H_{21}Cl_4N_3O_4$ (629.29) Calcd.: C 57.24, H 3.36, Cl 22.52, N 6.86. Found: C 56.96, H 3.79, Cl 23.24, N 6.84.

5-(3-Trifluoromethylphenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenyl-amino)-3-(4-methoxy-phenyl-iminomethylene)-pyridinium Perchlorate ***4d***

2.2 g **1b** and 2.5 g *p*-anisidine gave 2.53 g (74%) yellow crystals. m.p. 196 °C (decomp.); IR (KBr), ν(cm^{-1}): 1020, 1080, 1115, 1165, 1640; ^{1}H-NMR ($CDCl_3$, 200 MHz), δ(ppm): 13.94 (s, 1H, NH), 9.02 (s, 1H, C-5 H pyridine nucl.) 8.93 (d, 1H, C-2 H pyridine nucl. $^4J(^1H^1H)$ = 1.9 Hz), 7.77 (d, 1H, CH = N $^4J(^1H^1H)$ = 1.5 Hz), 7.60 (d, 2H, aromat.) $^3J(^1H^1H)$ = 9.0 Hz, 7.25–7.35 (m, 4H, aromat.), 7.21 (d, 2H, aromat. ^3J ($^1H^1H$) = 9.0 Hz), 6.88 (d, 2H, aromat. ^3J ($^1H^1H$) = 9.0 Hz), 6.87 (d, 2H, aromat. $^3J(^1H^1H)$ = 8.8 Hz), 6.63 (d, 2H, aromat. $^3J(^1H^1H)$ = 9.0 Hz), 6.53 (d, 2H, aromat. $^3J(^1H^1H)$ = 8.9 Hz), 3.77 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 3.63 (s, 3H, CH_3) MS: (FAB) (%): m/z = 584 (100) (M^+-$HClO_4$).

$C_{34}H_{29}ClF_3N_3O_7$ (684.03) Calcd.: C 59.69, H 4.27, N 6.14. Found: C 59.57, H 4.23, N 6.38.

1-(4-Aminophenyl)-4-(4-aminophenyl-amino)-3-(4-aminophenyl-iminomethylene)-5-(3-trifluoro-methylphenyl)-pyridinium Perchlorate ***4e***

2.2 g **1b** and 2,2 g *p*-phenylenediamine gave 2.1 g (66%) yellow crystals. m.p. 183 °C (decomp.); IR (KBr), ν(cm^{-1}): 1080, 110, 1125, 1170, 1640; ^{1}H-NMR (DMSO-D_6, 200 MHz), δ(ppm): 13.49 (s, 1H, NH), 9.06 (s, 1H, CH pyridine nucl.) 9.01 (s, 1H, pyridine nucl.), 8.42 (s, 1H, CH = N), 7.31–7.57 (m, 4H, aromat. 7.25 (d, 2H, aromat. $^3J(^1H^1H)$ = 8.4 Hz), 6.74 (d, 2H, aromat. $^3J(^1H^1H)$ = 8 Hz), 6.65 (d, 2H, aromat. $^3J(^1H^1H)$ = 8.6 Hz), 6.55 (d, 2H, aromat. ^3J ($^1H^1H$) = 8.4 Hz), 6.37 (s, 1H, aromat.), 6.15 (d, 2H, aromat. $^3J(^1H^1H)$ = 8.4 Hz), 5.70 (s, 2H, NH_2), 5.6 (s, 2H, NH_2), 5.09 (s, 2H, NH_2); MS: (FAB) (%): m/z = 638 (13) (M^+-1), 621 (19) (M^+-1-NH_3), 605 (100) (M^+-2×NH_3), 589 (49) (M^+-3×NH_3).

$C_{31}H_{26}ClF_3N_6O_4$ (639.00) Calcd.: C 58.26, H 4.10, N 13.15. Found: C 58.11, H 3.88, N 13.40.

7-Methoxy-2-(4-methoxyphenyl)-4-phenyl-10-aza-2-azonia-anthracene Perchlorate ***5***

0.3 g **4a** were dissolved in 50 ml of acetic acid and the mixture was refluxed for 15 minutes. After cooling to room temperature, the yellow solid compound was filtered and recrystallized from acetonitrile. Yield: 0.23 g (96%), m.p. 302 °C (decomp.); IR (KBr), ν(cm^{-1}): 1100, 1320, 1640; ^{1}H-NMR (DMSO-D_6, 400 MHz), δ(ppm): 10.706 (s, 1H, pyridine nucl.), 9.776 (s, 1H, pyridine nucl.), 9.185 (s, 1H, quinoline nucl.), 8.296–8.320 (d, 1H, quinoline nucl.), 8.003–8.035 (d, 1H, quinoline nucl.) 7.983 (s, 1H, quinoline nucl.), 8.123–8.145 (d, 2H, aromat.), 7.744–7.764 (m, 3H, aromat.), 8.172–8.195 (d, 4H, aromat.) 7.440–7.462 (d, 4H, aromat.), 4.116 (s, 3H, OCH_3), 4.037 (s, 3H, OCH_3); MS: (FAB): m/z = 394 (M^+-$HClO_4$).

$C_{26}H_{21}ClN_2O_6$ (492.89) Calcd.: C 63.35, H 4.29, Cl 7.19, N 5.68. Found: C 63.28, H 4.85, Cl 7.48, N 6.16.

2-(4-Methoxyanilinomethylene)-4-oxo-4-phenyl-1-butylidene-(4-methoxyanilinium) Perchlorate ***6a***

A mixture of 1.0 g **3a** and 1.3 g *p*-anisidine in 50 ml ethanol was refluxed for two hours to receive a homogenous solution which was allowed to cool to room temperature. Stored overnight, a yellow precipitate was deposited. This was filtered and recrystallized from ethanol to yield 1.1 g (74%) yellow crystals. m.p. 209 °C; IR (KBr), ν(cm^{-1}): 1270, 1620, 1670; MS: m/z = 400 (M^+-$HClO_4$).

$C_{25}H_{25}ClN_2O_7$ (500.95) Calcd.: C 59.94, H 5.03, Cl 7.08, N 5.59. Found: C 59.36, H 4.96, Cl 6.89, N 5.18.

2-(4-Chloroanilinomethylene)-4-oxo-4-phenyl-1-butylidene-(4-chloroanilinium) Perchlorate ***6b***

A mixture of 1.0 g **3a** and 1.4 g *p*-chloroaniline in 50 ml ethanol was refluxed for about two hours to obtain a homogenous solution which was allowed to cool to room temperature. Stored overnight, a yellow precipitate was deposited. This was filtered and recrystallized from ethanol to yield 1.3 g (83%) yellow crystals. m.p. 220 °C; IR (KBr), ν(cm^{-1}): 1100, 1560, 1630, 1650, 3100, 3200; ^{1}H-NMR (DMSO-D_6, 400 MHz), δ(ppm): 11.097 (s, 1H, NH), 8.573 (s, 1H, CH), 8.138 (s, 1H, CH), 7.655–7.677 (m, 4H, aromat.), 7.474–7.503 (m, 4H, aromat.), 7.058–7.080 (m, 5H, aromat.), 3.884 (s, 2H, CH_2); MS: m/z = 410 (M^+-$HClO_4$)

$C_{23}H_{19}Cl_3N_2O_5$ (509.74) Calcd.: C 54.19, H 3.76, Cl 20.86, N 5.50. Found: C 54.43, H 3.97, Cl 21.05, N 5.55.

*3-Phenacyl-1*H*-1.5-benzodiazepinium Perchlorate* ***7***

A suspension of 1.0 g **3a** in 50 ml ethanol was added to a solution of 0.4 g *o*-phenylenediamine in 20 ml ethanol and 5 ml 70% perchloric acid. The mixture was stirred and heated to 50 °C to obtain a homogenous solution with a deep violet color, allowed to cool to room temperature and kept overnight in a refrigerator at about –25 °C. The black-violet crystals which were deposited were filtered and washed with cold ether to yield 0.9 g (81%) crystals. m.p. 198 °C; IR (KBr), ν(cm^{-1}): 1090, 1610, 1650, 3100, 3300; ^{1}H-NMR (DMSO-D_6, 80 MHz), δ(ppm): 10.640 (s, 2H, 2×NH), 7.289 (s, 2H, 2×CH, azepine nucl.), 7.043–7.7.190 (m, 5H, C_6H_5), 6.339–6.895 (m, 4H, C_6H_4), 3.775 (s, 2H, CH_2); MS: m/z = 263 (M^+-$HClO_4$).

$C_{17}H_{15}ClN_2O_5$ (362.74) Calcd.: C 56.28, H 4.17, Cl 9.77, N 7.72. Found: C 56.03, H 4.31, Cl 9.80, N 7.65.

Acknowledgments. We would like to thank the Deutsche Forschungsgemeinschaft (DFG) and the Fond der Chemischen Industrie for financial support.

References and Notes

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