J. prakt. Chem. 338 (1996) 718–724

Journal für praktische Chemie
Chemiker-Zeitung

Ring Opening Reactions of Pyridinium- and Phosphonium Betaines of Squaric Acid in Alkaline Media

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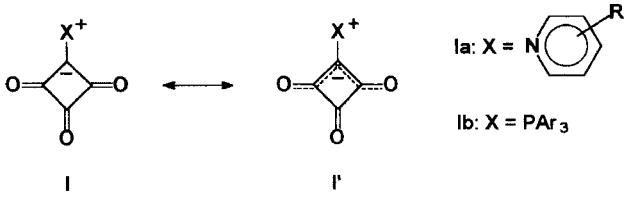
Received February 28th, 1996 respectively June 12th, 1996

Abstract. Pyridiniumtrioxocyclobutylides **1** bearing electron-donating substituents undergo ring opening reactions at the four-membered ring in alkaline media. The structure of one of the resulting bisacyl ylides **3** is confirmed by X-ray analysis. In acidic media **3** are easily hydrolysed forming quaternary pyridinium salts of pyruvic acid **6**; the existence of a stable *gem*-diol form **5** in the crystalline state is also proved by X-ray analysis. Triphenylphosphoniumtrioxocyclobutylide (**8**) gives the bisacyl ylide **9**, which is hydrolysed to (triphenylphosphor-anylidene)pyruvic acid (**10**).

Reaction of squaric acid with pyridines or triarylphosphanes in acetic anhydride yields trioxocyclobutylides represented by the general formula **I** [1a]. Similar processes use squaric acid dichloride as starting material [1b – 1f]. A large number of compounds have been prepared by these methods [1g]. The negative charge is effectively stabilized by the carbonyl groups adjacent to the ylidic carbon, as represented by the resonance structure **I'**. Because of the charge delocalisation, all pyridinium and phosphonium betaines of squaric acid are stable compounds.



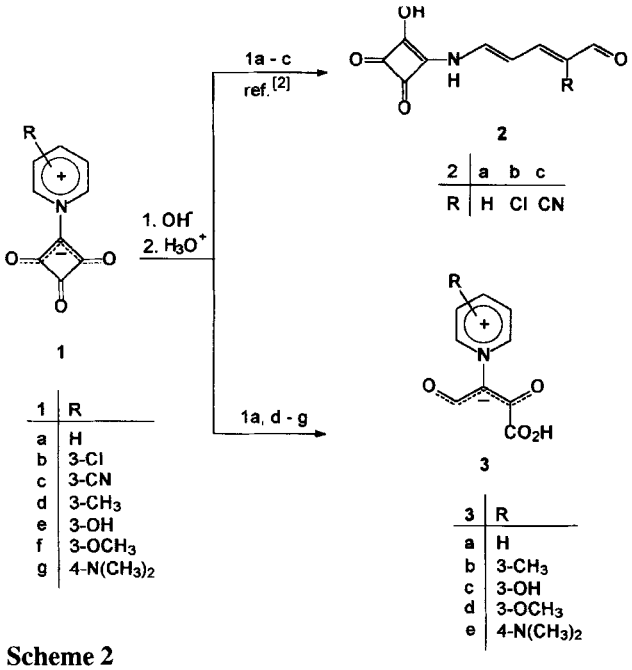
I I'

Scheme 1

The synthetic utility of the pyridinium betaines **Ia** derives primarily from the reactivity of the electron-deficient centres at C-2/C-6 of the heterocycle and C-3 of the four-membered ring. Nucleophilic addition of a hydroxide ion at C-2 of the pyridinium ring is followed by ring opening of the heterocycle [2], whereas reactions at C-3 of the four-membered ring with hydrazines yielding hydrazones [1d] and secondary amines giving squaraines [1e] are described. In contrast, the chemistry of the phosphonium betaines **Ib** is obviously hitherto unknown.

Whereas pyridinium betaines of squaric acid are only slightly soluble in polar organic solvents and water, they dissolve readily in aqueous alkaline solutions. As described in a preceding communication [2], in this medium some betaines bearing electron-withdrawing groups at C-3 (**1b, c**) undergo regioselective ring opening reactions at C-2 of the heterocycle. The resulting 5-aminoglutaconaldehyde derivates **2** are precipitated from the solutions by addition of strong acids. The unsubstituted pyridinium betaine **1a** reacts in the same manner, but with lower yield.

In order to establish the scope and limitations of this reaction, pyridinium betaines with electron-donating substituents were also examined. On treating with aqueous hydroxide solutions, 2- and 4-methylpyridinium betaines yielded only black decomposition products. In contrast, the ring-opened bisacyl ylides **3** were obtained by slow acidification of the alkaline solutions of the betaines **1a, d–g**.



Scheme 2

These experimental results may be explained as follows: Whereas in the derivatives with electron-withdrawing substituents (**1b**, **c**) C-2 of the heterocycle exhibits the greatest reactivity to nucleophiles, in the betaines with electron-donating groups (**1d**–**g**) the heterocycle is deactivated, and C-3 of the four-membered ring becomes the preferentially attacked electron-deficient centre. The initial addition of a hydroxide ion is followed by cleavage of the 2,3-bond. Similar ring opening reactions in alkaline solutions have been reported for some phenyl-substituted cyclobutenediones [3].

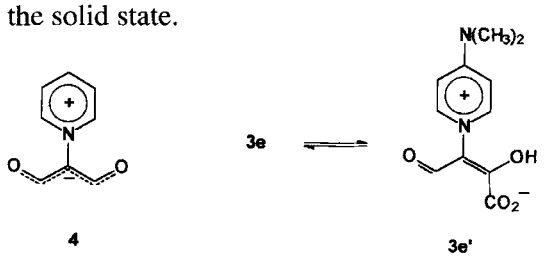
Depending on the reaction time, the unsubstituted pyridinium betaine **1a** yielded the glutaconaldehyde **2a** or the bisacyl ylide **3a**. Immediate strong acidification of a freshly prepared solution of **1a** afforded **2a**, whereas after standing overnight **3a** was isolated as the only product. Controlling the reaction course by TLC demonstrated the presence of two substances in the alkaline solution some minutes after preparation. Four hours later, however, only one product was detected. Obviously the anion of the primary product **2a** is transformed into the salt of the final product **3a**, probably via recyclization in the alkaline medium.

The ylides **3** are readily soluble in polar organic solvents such as methanol, ethanol and DMF. From mixtures of organic solvents with water they crystallize as monohydrates. The crystal water may be removed by drying at ca. 50 °C *in vacuo*. The anhydrous compounds are stable on storage in a desiccator; in contact with aerial moisture, however, decomposition may occur.

With ferric chloride, aqueous solutions of **3** give brown-red complexes, and with some heavy metal ions such as copper(II), nickel(II) and zinc, sparingly soluble salts are precipitated.

The structure of **3** follows from the spectroscopic properties. The ^{1}H NMR-spectra are characterized by a singlet of the formyl proton at δ = ca. 9.2; for comparison, the spectrum of the diformyl methylide **4** exhibits a signal at δ = 8.91 [4]. In the ^{13}C NMR-spectra of **3** the signal of the ylidic carbon appears at δ = ca. 122 (**3a**: $^2J_{C,H}$ = 31.3 Hz), or δ = 124 in the case of **4** ($^2J_{C,H}$ = 28.8 and 30.7 Hz). The resonance in the carbonyl region at δ = ca. 175 is assigned to the formyl group (**4**: δ = 177). These NMR-spectroscopic data rule out cyclic forms such as those described for some γ-aldehydo- and γ-ketocarboxylic acids [5].

The IR-spectra of **3** show strong (**3a**, **b**, **d**) or weak (**3c**) absorptions of the carboxyl group at ca.1735 cm^{-1}; this absorption is missing in the spectrum of **3e**, implying that a tautomeric form such as **3e'** is predominant in the solid state.



Scheme 3

In order to exclude possible cyclic forms for the crystalline state, an X-ray analysis was performed on the monohydrate of **3a** (see Fig.1): The carbon atom of the ylide moiety, C6, displays planar geometry (mean deviation 0.01 Å). Bond lengths are consistent with the delocalisation proposed in scheme 2, with C6–C9 1.409 (2), C6–C7 1.401(2), (cf. C7–C8, a pure single bond, 1.543(2)), C7–O2 1.246(2), C9–O1 1.240(2) Å (cf. double bond C8–O4 1.190(2) Å). The N–C6 bond length is 1.454(2) Å. The wide angle C9–C6–C7 128.3(2)° reflects the influence of the electron-withdrawing N$^+$ group. The pyridinium ring is rotated by 70° out of the plane of C6,7,8,9,O1,2.

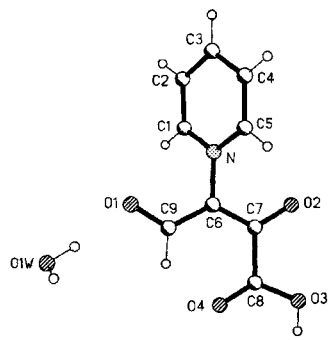


Fig. 1 The formula unit of compound **3a** · H_2O in the crystal. Radii are arbitrary.

The crystal packing (Fig. 2) is determined by strong hydrogen bonding contacts. The water molecule acts as an H bond donor to O1 (O···O: 2.69 Å) and O2 (O···O: 2.76 Å) and as acceptor from O3 (O···O: 2.52 Å). The extended structure consists of two corrugated interpenetrating sheets.

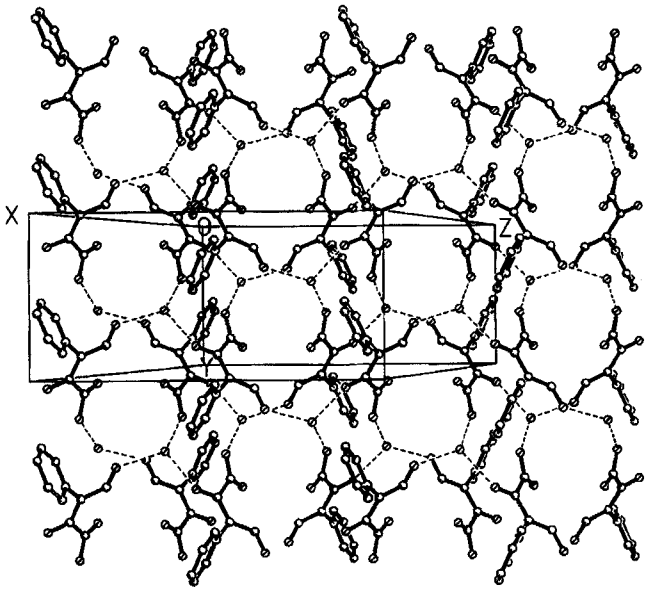
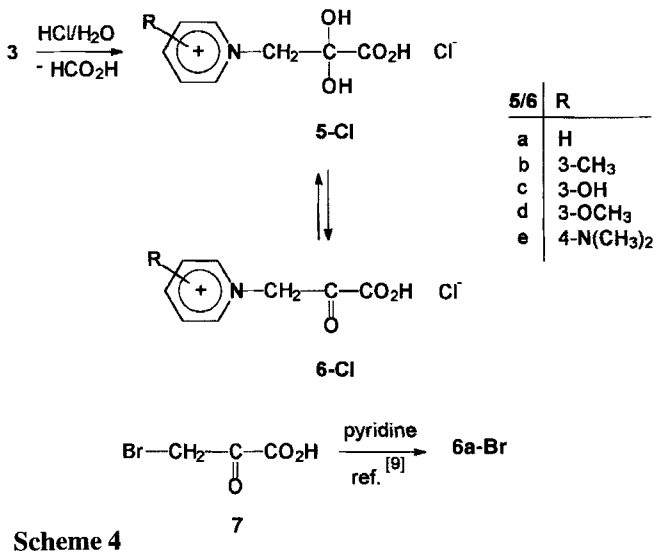


Fig. 2 Packing diagram of **3a** · H_2O (H atoms omitted). Hydrogen bonds are indicated by dashed lines

As described by Kröhnke [6], in aqueous solutions in the presence of strong acids bisacylpyridinium ylides lose one substituent giving pyridinium salts. Accordingly, all compounds **3** underwent hydrolysis in strongly acidic media at room temperature with elimination of formic acid (identified by reduction of silver nitrate), whereas formation of oxalic acid was not observed. The resulting pyridinium salts crystallized as mono- or dihydrates; on drying the latter *in vacuo* at room temperature the monohydrates were obtained. Further drying at ca. 80 °C resulted in partial liquefaction of the compounds; exact melting points could not be determined. These observations may be explained by the existence of two forms of the resulting pyruvic acid derivates: in the solid state only the *gem*-diol form **5** is present, whereas at higher temperatures and in solution dehydration to the keto form **6** occurs. (Scheme 4)

The existence of a stable *gem*-diol in the solid state was proved by an X-ray analysis of the monohydrate of **5a** –Cl (see Fig. 3): In the absence of an ylidic structural element, the bond lengths N–C6 1.472(2), C6–C7 1.535(2) Å can be regarded as normal. The bond lengths in the *gem*-diol moiety are C7–O3 1.407(2), C7–O4 1.390(2) Å. The conformation about C7–C8 is *gauche*, with O1–C8–C7–O3 66°.



Scheme 4

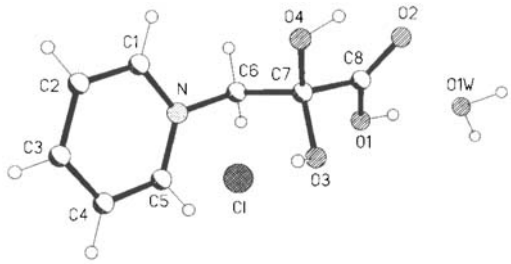


Fig. 3 The formula unit of compound **5a** –Cl · H_2O in the crystal. Radii are arbitrary.

The packing diagram (Fig. 4) shows anions, cations and water linked into sheets by hydrogen bonding. The chloride accepts H bonds from O3 (Cl···O: 3.14 Å), and two water molecules (Cl···O: 3.14 and 3.15 Å); the water molecule accepts a short H bond from O1 (O···O: 2.56 Å), which in turn accepts a weak H bond from O4 (O···O: 3.00 Å).

It is well known that most α-keto acids exist in equilibrium with the *gem*-diol form. The degree of hydration strongly depends on the inductive effect of the substituent: Electron-withdrawing groups promote nucleophilic attack by water, electron-donating groups have the opposite effect [7].

As shown by the NMR spectra of **5** (the spectroscopic data of the monohydrates resemble those of **5**), in solution the keto form **6** is also present. In the ^1H NMR spectra there are two distinct methylene signals at δ = ca.

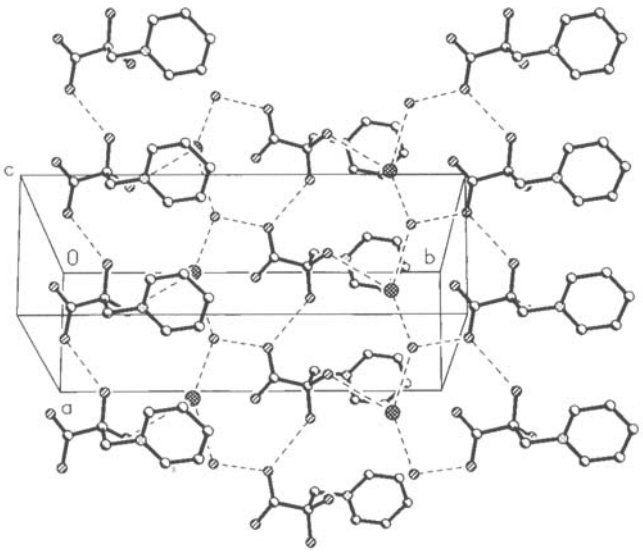


Fig. 4 Packing diagram of **5a** – Cl · H_2O (H atoms omitted). Hydrogen bonds are indicated by dashed lines.

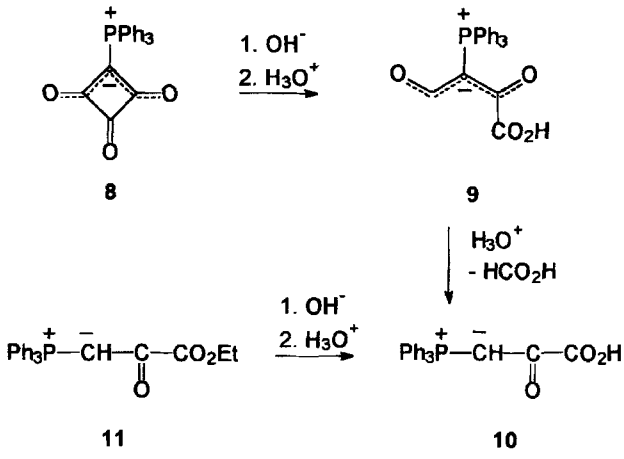
4.8 (*gem*-diol form) and δ = ca. 6.1 (keto form **6**, exchanges with deuterium oxide). The ratio of hydrated to nonhydrated form in solutions of α-keto acids may be determined by integration [7]: shortly after preparation 50–60% was in the *gem*-diol form **5**, and after 24 h this ratio was nearly unchanged.

The ^{13}C NMR spectra of **5/6** display, besides a signal of the carbonyl at δ = ca. 186, a signal at δ = ca. 91, which is characteristic of a *gem*-diol carbon [8]. The other carbon atoms also give rise to two distinct peaks, the difference between the two forms being max. 1 ppm for the pyridinium resonances.

Because of the sensitivity of **3** to hydrolysis in acidic media, the pyridinium salts **5** were always formed as by-products during the preparation of **3** and could be extracted from the dry residues of the reaction mixtures with methanol. The direct preparation of **5** without isolation of **3** was possible by strong acidification of the alkaline solutions of **1** and storage of the reaction mixtures at room temperature for some hours.

Whereas the *gem*-diols **5** were until now unknown, the preparation of **6a**-Br from bromopyruvic acid (**7**) and pyridine has been described [9]. The unstable product was characterised only by an elemental analysis that diverged distinctly from the calculated values. The described procedure gave a viscous yellow oil consisting of several compounds, as found by TLC. In the ^1H NMR spectrum the signals of the *gem*-diol **5a** and the ketone **6a** were observed, with low intensity. The analogous treatment of bromopyruvic acid with 4-dimethylaminopyridine gave a solid product consisting mainly of 4-dimethylaminopyridinium bromide. Obviously the direct quaternisation of pyridines with bromopyruvic acid is difficult because of side reactions.

Upon heating with sodium hydroxide solution, the triphenylphosphonium ylide **8** underwent ring opening in the same manner as described for the pyridinium ylides, giving rise to the formation of 2,4-dioxo-3-(triphenylphosphoranylidene)butanoic acid (**9**). Although up to 20% triphenylphosphine oxide was extracted from the reaction mixture, no further by-products containing a cyclobutenedione moiety could be detected.



Scheme 5

In the ^1H NMR spectrum of **9** the formyl proton displays a doublet by coupling with the ^{31}P nucleus ($^3J_{P,H}$ = 10.0 Hz). The proton decoupled ^{13}C NMR spectrum shows the ylidic carbon as a doublet at δ = 82.4 ($J_{C,P}$ = 100.1 Hz); in the $^{13}C/^1H$ coupled spectrum it is split into a double doublet with a coupling constant of $^2J_{C,H}$ = 24.2 Hz; this value is in the same order of magnitude as evaluated for the pyridinium betaines **3** and **4** (see above). Hence, the structural moiety HC(=O)–C=PPh_3 is definitively proved.

Refluxing of the phosphorus betaine **9** in hydrochloric acid afforded the ylide **10** as the only product apart from some triphenylphosphine oxide. **10** was also obtained by alkaline hydrolysis of the ester **11**.

J. G. thanks the Hüls AG for a generous gift of squaric acid and Prof. Dr. L. Ernst for NMR advice. P. G. J. thanks the Fonds der Chemischen Industrie for financial support.

Experimental

Melting points (uncorrected): Linström apparatus. – UV/VIS: Philips PU 8730, solvent: ethanol. – IR (KBr): Pye Unicam SP 3-100 and SP 3-200. – ^1H and ^{13}C NMR: Bruker AM-400 (400.13 MHz ^1H, 100.61 MHz ^{13}C), solvent: [D_6]DMSO, chemical shifts are reported in δ values relative to TMS. The multiplicity of the ^{13}C NMR signals was determined by DEPT

experiments. – ^{31}P NMR: Bruker AC 200 (81.02 MHz), solvent: [D_6]DMSO, external standard 85% phosphoric acid. – MS: Finnigan MAT 8430. – Elemental analyses: Carlo Erba CHNO Elemental Analyzer 1106–1 and 1106–2.

Pyridiniumtrioxocyclobutylides 1

Pyridiniumtrioxocyclobutylide (**1a**)[1a], *3-Methylpyridiniumtrioxocyclobutylide* (**1d**) [1a], *3-Hydroxypyridiniumtrioxocyclobutylide* (**1e**) [1f] and *4-Dimethylaminopyridiniumtrioxocyclobutylide* (**1g**) [1e] were prepared by literature procedures.

3-Methoxypyridiniumtrioxocyclo-butylide (**1f**)
From 11.41 g (0.1 mol) squaric acid and 10.91 g (0.1 mol) 3-methoxypyridine [10] by the general procedure described in ref. [1a]. Orange crystals from DMSO/methanol, yield 13.8 g (67%), *m.p.* 205–207 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1785 cm^{-1}, 1735 (C=O). – ^{1}H NMR: δ = 4.08 (s, 3H, CH_3), 8.05–8.40 (m, 2H), 8.94–9.13 (m, 2H, arom. H). – $C_{10}H_7NO_4$ (205.2): calcd. C 58.54, H 3.44, N 6.83; found C 58.55, H 3.49, N 6.66.

General procedure for the preparation of the bisacyl ylides 3

10 mmol of the pyridinium betaine **1** were dissolved in 20 ml of 1 M potassium hydroxide solution (**1g** requires slight shaking). After storage for at least 4 h at room temperature, the mixtures were cooled to 0 °C in an ice-bath. 25% hydrochloric acid was added dropwise with stirring, until precipitation of the products **3** was complete. After standing in an ice-bath for 1 h, the products were collected, washed with cold 3% hydrochloric acid, dried over KOH in vacuo and recrystallized.

Pyridinium-(2-carboxy-1-formyl-2-oxoethylide) (**3a**)
Pale yellow crystals from methanol/water, yield 1.35 g (70%), *m.p.* 193–194 °C (dec.).– IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (OH), 1735 (COOH), 1630 (C=C). – UV: λ_{max} (lg ε) = 262 nm (4.20), 357 (3.31). – ^{1}H NMR: δ = 8.07–8.10 (m, 2H), 8.48 –8.52 (m, 1H), 8.71–8.72 (m, 2H, arom. H), 9.20 (s, 1H, CH=O), 11.92 (br. s, 1H, OH). – ^{13}C NMR: δ = 123.14 (s, ylidic C), 128.00 (d), 145.11 (d), 148.07 (d, arom. C), 168.40 (s, COOH), 175.58 (s, C=O), 176.18 (d, CH=O). – MS (70 eV): *m/z* (%) = 193 (26) [M$^+$], 165 (42) [M$^+$ – CO], 148 (55) [M$^+$ – COOH], 120 (100) [148 – CO]. – $C_9H_7NO_4$ (193.2): calcd. C 55.96, H 3.65, N 7.25; found C 55.93, H 3.62, N 7.12.

3-Methylpyridinium-(2-carboxy-1-formyl-2-oxoethylide) (**3b**)
Yellowish crystals from 2-propanol/water, yield 1.10 g (53%), *m.p.* 183–184 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1} (OH), 1735 (COOH), 1630 (C=C). – UV: λ_{max} (lg ε) = 266 nm (4.24), 348 (3.32). – ^{1}H NMR: δ = 2.49 (s, 3H, CH_3), 7.96–8.00 (m, 1H), 8.34–8.36 (m, 1H), 8.50–8.51 (m, 1H), 8.60 (s, 1H, arom. H), 9.17 (s, 1H, CH=O), 10.50 (br. s, 1H, OH). – ^{13}C NMR: δ = 17.51 (q, CH_3), 122.17 (s, ylidic C), 126.36 (d), 137.69 (s), 144.55 (d), 144.59 (d), 146.49 (d, arom. C), 167.43 (s, COOH), 174.57 (s, C=O), 175.10 (d, CH=O). – MS (70 eV): *m/z* (%) = 207 (18) [M$^+$], 179 (37) [M$^+$ – CO], 162 (47) [M$^+$ – COOH], 134 (100) [162 – CO]. – $C_{10}H_9NO_4$ (207.2): calcd. C 57.97, H 4.38, N 6.76; found C 57.97, H 4.34, N 6.85.

3-Hydroxypyridinium-(2-carboxy-1-formyl-2-oxoethylide) (**3c**)
Grey powder from 2-propanol/water, yield 1.95 g (93%), *m.p.* 188–190 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1}, 3250 (OH), 1750 (COOH), 1615 (C=C). – UV: λ_{max} (lg ε) = 255 nm (3.69), 334 (3.47). – ^{1}H NMR: δ = 3.63 (br. s, 1H, OH), 7.89–7.91 (m, 2H), 8.12 (s, 1H), 8.16–8.17 (m, 1H, arom. H), 9.12 (s, 1H, CH=O), 11.68 (br. s, 1H, OH). – ^{13}C NMR: δ = 122.15 (s, ylidic C), 127.50 (d), 130.35 (d), 134.92 (d), 138.38 (d), 156.16 (s, arom. C), 167.53 (s, COOH), 174.73 (s, C=O), 175.12 (d, CH=O). – MS (DCI, NH_3, pos.): *m/z* (%) = 191 (3) [M$^+$ – H_2O], 96 (100) [$C_5H_6NO^+$]. – $C_9H_7NO_5$ (209.2): calcd. C 51.68, H 3.37, N 6.70; found C 51.33, H 3.37, N 6.57.

3-Methoxypyridinium-(2-carboxy-1-formyl-2-oxoethylide) (**3d**)
Yellowish powder from methanol/water, yield 1.18 g (53%), *m.p.* 192–193 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1} (OH), 1730 (COOH), 1645 (C=C). – UV: λ_{max} (lg ε) = 273 nm (4.26), 348 (3.36). – ^{1}H NMR: δ = 3.98 (s, 3H, CH_3), 7.98–8.02 (m, 1H), 8.14–8.17 (m, 1H), 8.29–8.31 (m, 1H), 8.46 (s, 1H, arom. H), 9.18 (s, 1H, CH=O), 11.85 (br. s, 1H, OH). – ^{13}C NMR: δ = 57.20 (q, CH_3), 122.53 (s, ylidic C), 127.32 (d), 129.11 (d), 135.00 (d), 139.82 (d), 157.45 (s, arom. C), 167.40 (s, COOH), 174.42 (s, C=O), 175.15 (d, CH=O). – MS (70 eV): *m/z* (%) = 223 (41) [M$^+$], 195 (62) [M$^+$ – CO], 178 (95) [M$^+$ – COOH], 150 (100) [178 – CO]. – $C_{10}H_9NO_5$ (223.2): calcd. C 53.82, H 4.06, N 6.28; found C 53.64, H 4.05, N 6.29.

4-Dimethylaminopyridinium-(2-carboxy-1-formyl-2-oxoethylide) (**3e**)
Pale yellow crystals from methanol, yield 2.2 g (93%), *m.p.* 185–186 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3150 cm^{-1} (OH), 1690 (sh, COOH), 1645 (C=C). – UV: λ_{max} (lg ε) = 278 nm (4.47). – ^{1}H NMR: δ = 3.19 (s, 6H, CH_3), 5.45 (br. s, 1H, OH), 6.94 (d, 2H), 7.84 (d, 2H, arom. H), 9.05 (s, 1H, CH=O). – ^{13}C NMR: δ = 39.63 (q, CH_3), 106.78 (d, arom. C), 120.23 (s, ylidic C), 144.98 (d), 155.40 (s, arom. C), 168.30 (s, COOH), 175.90 (s, C=O), 176.20 (d, CH=O). – MS (FAB, neg, 2-nitrobenzyl alcohol): *m/z* = 235 [M$^-$ – H]. – $C_{11}H_{12}N_2O_4$ (236.2): calcd. C 55.93, H 5.12, N 11.86; found C 55.88, H 5.12, N 11.62.

Structure determination of compound 3a · H_2O

Crystal data: $C_9H_9NO_5$, M_ρ = 211.17, monoclinic, space group *C2/c*, *a* = 18.506(4), *b* = 7.134(2), *c* = 14.929(3) Å, β = 108.93(2)°, *V* = 1864.2 Å^3, *Z* = 8, D_x = 1.505 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 0.13 mm^{-1}, *T* = –130 °C. Data collection and reduction: A yellow prism 0.65 × 0.35 × 0.2 mm was mounted in inert oil. Data were collected to $2\Theta_{max}$ 55° on a Stoe STADI-4 diffractometer fitted with a Siemens LT-2 low temperature attachment. Of 3251 measured data, 2147 were unique (R_{int} 0.018). Structure solution and refinement: The structure was solved by direct methods and refined anisotropically on F^2 using all reflections (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included as follows: water H with distance restraints, OH rigid, others riding. The final $wR(F^2)$ was 0.117 for 143

parameters, conventional $R(F)$ 0.045. S = 1.02; max. Δ/σ < 0.001; max. $\Delta\rho$ 0.59 e Å^{-3}.

Pyridinium-(1-formyl-2-oxoethylide) (4)

Preparation by literature procedure [4]. – ^{13}C NMR: δ = 123.87 (s, ylidic C), 126.85 (d), 142.94 (d), 144.82 (d, arom. C), 177.05 (d, CH=O).

General procedure for the preparation of the pyridinium salts 5

10 mmol of the bisacyl ylides **3** were dissolved in 10 ml of 25% hydrochloric acid. After standing at room temperature for one day and evaporation of volatile components the residues were recrystallized from acetone/25% hydrochloric acid. The products were dried at room temperature over KOH in vacuo.

(2-Carboxy-2,2-dihydroxyethyl)pyridinium chloride (**5a**)
Yellowish needles, yield 1.60 g (73%), *m.p.* 114–116 °C. – IR (KBr): $\tilde{\nu}$ = 3500 cm^{-1}, 2720, 2560, 2440 (OH), 1720 (COOH), 1625 (C=C). – UV: λ_{max} (lg ε) = 261 nm (4.03). – ^{1}H NMR: δ = 4.89 (s, 2H, CH_2-C(OH)$_2$), 6.19 (s, 2H, CH_2-C=O), 7.16 (br. s, 6H, OH, H_2O), 8.16–8.19 (m, 2H), 8.26–8.30 (m, 2H), 8.65–8.69 (m, 1H), 8.72–8.77 (m, 1H), 8.99–9.02 (m, 4H, arom. H). – ^{13}C NMR: δ = 65.02 (t, CH_2–C(OH)$_2$), 66.82 (t, CH_2–C=O), 90.82 (s, C(OH)$_2$), 126.87 (d), 127.82 (d), 146.00 (d), 146.10 (d), 146.52 (d), 146.64 (d, arom. C), 159.60 (s), 170.93 (s, COOH), 186.06 (s, C=O). – MS (FAB, pos., glycerol): *m/z* = 184 [cation], 166 [184 – H_2O], 138 [166 – CO]. – $C_8H_{10}ClNO_4$ (219.6): calcd. C 43.75, H 4.59, N 6.38; found C 43.52, H 4.58, N 6.28.

(2-Carboxy-2,2-dihydroxyethyl)-3-methylpyridinium chloride (**5b**)
Colorless crystals, yield 1.29 g (55%), *m.p.* 185–187 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 3160, 2760 (OH), 1730 (COOH), 1635 (C=C). – UV: λ_{max} (lg ε) = 268 nm (4.06). – ^{1}H NMR: δ = 2.50 (s, 3H), 2.52 (s, 3H, CH_3), 4.83 (s, 2H, CH_2–C(OH)$_2$), 6.14 (s, 2H, CH_2–C=O), 7.11 (br. s, 6H, OH, H_2O), 8.05–8.08 (m, 1H), 8.15–8.19 (m, 1H), 8.51 (d, 1H), 8.58 (d, 1H), 8.84–8.85 (m, 2H), 8.93 – 8.94 (m, 2H, arom. H). – ^{13}C NMR: δ = 17.82 (q), 17.90 (q, CH_3), 64.88 (t, CH_2–C(OH)$_2$), 66.58 (t, CH_2–C=O), 90.89 (s, C(OH)$_2$), 126.22 (d), 127.15 (d), 137.26 (s), 138.25 (s), 143.47 (d), 143.98 (d), 145.39 (d), 146.04 (d), 146.27 (d), 146.84 (d, arom. C), 159.59 (s), 170.92 (s, COOH), 186.10 (s, C=O). – MS (FAB, pos., glycerol): *m/z* = 198 [cation], 180 [198 – H_2O], 152 [180 – CO]. – $C_9H_{12}ClNO_4$ (233.7): calcd. C 46.27, H 5.18, N 5.99; found C 46.26, H 5.22, N 5.87.

(2-Carboxy-2,2-dihydroxyethyl)-3-hydroxypyridinium chloride (**5c**)
Colorless crystals, yield 1.74 g (74%), *m. p.* 145–147 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1}, 2920 (OH), 1730 (COOH), 1620 (C=C). – UV: λ_{max} (lg ε) = 224 nm (3.97), 295 (4.05). – ^{1}H NMR: δ = 4.75 (s, 2H, CH_2–C(OH)$_2$), 5.99 (s, 2H, CH_2–C=O), 7.47 (br. s, 6H, OH, H_2O), 7.91–7.95 (m, 1H), 8.00–8.04 (m, 1H), 8.13–8.15 (m, 1H), 8.18–8.21 (m, 1H), 8.37–8.42 (m, 2H), 8.48–8.51 (m, 2H, arom. H), 12.18 (br. s, 2H, OH). – ^{13}C NMR: δ = 65.24 (t, CH_2–C(OH)$_2$), 66.86 (t, CH_2–C=O), 91.00 (s, C(OH)$_2$), 127.22 (d), 128.20 (d), 131.71 (d), 132.30 (d), 134.04 (d), 134.78 (d), 136.84 (d), 137.46 (d), 156.17 (s), 156.94 (s, arom. C), 159.64 (s), 170.96 (s, COOH), 185.81 (s, C=O). – MS (FAB, pos., glycerol): *m/z* = 200 [cation], 182 [200 – H_2O], 154 [182 – CO]. – $C_8H_{10}ClNO_5$ (235.6): calcd. C 40.78, H 4.28, N 5.94; found C 40.80, H 4.23, N 5.72.

(2-Carboxy-2,2-dihydroxyethyl)-3-methoxypyridinium chloride (**5d**)
Colorless crystals, yield 1.39 g (56%), *m.p.* 111–115 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3360–3120 cm^{-1}, 2560 (OH), 1750 (COOH), 1635 (C=C). – UV: λ_{max} (lg ε) = 224 nm (4.08), 292 (4.10). – ^{1}H NMR: δ = 4.01 (s, 6H, CH_3), 4.88 (s, 2H, CH_2–C(OH)$_2$), 6.18 (s, 2H, CH_2–C=O), 6.80 (br. s, 6H, OH, H_2O), 8.07–8.11 (m, 1H), 8.17–8.21 (m, 1H), 8.30–8.33 (m, 1H), 8.36–8.39 (m, 1H), 8.61 (s, 1H), 8.63 (s, 1H), 8.93 (d, 1H), 8.97 (d, 1H, arom. H). – ^{13}C NMR: δ = 57.40 (q), 57.48 (q, CH_3), 65.06 (t, CH_2–C(OH)$_2$), 66.94 (t, CH_2–C=O), 90.97 (s, C(OH)$_2$), 127.23 (d), 128.22 (d), 130.54 (d), 131.28 (d), 133.89 (d), 134.78 (d), 138.61 (d), 139.15 (d), 156.93 (s), 157.58 (s, arom. C), 159.57 (s), 170.92 (s, COOH), 185.88 (s, C=O). – MS (FAB, pos., glycerol): *m/z* = 214 [cation], 196 [214 – H_2O], 168 [196 – CO]. – $C_9H_{12}ClNO_5$ (249.7): calcd. C 43.30, H 4.84, N 5.61; found C 43.29, H 4.93, N 5.50.

(2-Carboxy-2,2-dihydroxyethyl)-4-dimethylaminopyridinium chloride (**5e**)
Fine yellowish crystals, yield 1.89 g (72%), *m. p.* 162–165 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1}, 3180, 2700, 2550 (OH), 1720 (COOH), 1640 (C=C). – UV: λ_{max} (lg ε) = 290 nm (4.68). – ^{1}H NMR: δ = 3.19 (s, 6H), 3.22 (s, 6H, CH_3), 4.40 (s, 2H, CH_2–C(OH)$_2$), 5.65 (s, 2H, CH_2–C=O), 6.48 (br. s, 6H, OH, H_2O), 7.02 (d, 2H), 7.12 (d, 2H), 8.13 (d, 2H), 8.18 (d, 2H, arom. H). – ^{13}C NMR: δ = 39.93 (q), 40.14 (q, CH_3), 61.41 (t, CH_2–C(OH)$_2$), 62.95 (t, CH_2–C=O), 91.48 (s, C(OH)$_2$), 106.58 (d), 107.39 (d), 143.02 (d), 143.78 (d), 156.04 (s, arom. C), 159.95 (s), 171.33 (s, COOH), 187.87 (s, C=O). – MS (FAB, pos., glycerol): *m/z* = 227 [cation], 209 [227 – H_2O], 181 [209 – CO], 165 [209 – CO_2]. – $C_{10}H_{15}ClN_2O_4$ (262.7): calcd. C 45.72, H 5.76, N 10.66; found C 45.54, H 5.82, N 10.49.

Structure determination of compound 5a · H_2O

Crystal data: $C_8H_{12}ClNO_5$, M_p = 237.64, monoclinic, space group $P2_1/n$, a = 5.2173(10), b = 16.376(2), c = 12.252(2) Å, β = 99.477(14)°, V = 1032.5 Å^3, Z = 4, D_x = 1.529 Mg m^{-3}, μ = 0.37 mm^{-1}, T = –130 °C. Data collection and reduction: Brownish prism 0.9 × 0.7 × 0.6 mm, 3568 data, 2371 unique (R_{int} 0.028). Structure solution and refinement: $wR(F^2)$ 0.117 for 148 parameters, $R(F)$ 0.038, S 1.07, max. $\Delta\rho$ 0.63 e Å^{-3}. All other details as above (compound **3a** · H_2O).
Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 404187 (**3a**), 404188 (**5a**).

2,4-Dioxo-3-(triphenylphosphoranylidene)butanoic acid (**9**)

3.58 g (10 mmol) triphenylphosphoranylidecyclobutanetri-

one (**8**) [1a] were refluxed with 20 ml of 1 M sodium hydroxide solution until the educt was completely dissolved (ca. 30 min). After cooling to room temperature, the turbid mixture was extracted with dichloromethane (3 × 15 ml) to remove thiphenylphosphine oxide. The product was precipitated by dropwise addition of 25% hydrochloric acid to the stirred and ice-cooled aqueous layer. After standing in an ice-bath for 1 h, the precipitate was collected, washed with cold water and recrystallized from acetonitrile/dichloromethane to give colorless prisms; yield 2.48 g (66%), *m. p.* 187–188 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (OH), 1720 (COOH), 1670 (C=O). – ^1H NMR: δ = 7.64–7.77 (m, 15H, arom. H), 8.72 (d, J = 10.0 Hz, 1H, CH=O), 13.20 (br. s, 1H, OH). – ^{13}C NMR: δ = 82.38 (d, J = 100.1 Hz, ylidic C), 122.08 (d, J = 91.2 Hz), 129.38 (dd, J = 12.7 Hz), 133.26 (dd, J = 2.9 Hz), 133.41 (dd, J = 10.4 Hz, arom. C), 167.81 (d, J = 13.8 Hz, COOH), 183.33 (dd, J = 15.3 Hz, CH=O), 185.51 (d, J = 5.5 Hz, C=O). – ^{31}P NMR: δ = 16.7. – MS (70 eV): *m/z* (%) = 376 (15) [M^+], 347 (22) [M^+ – CHO], 331 (38) [M^+ – COOH], 303 (100) [331 – CO]. – $C_{22}H_{17}O_4P$ (376.4): calcd. C 70.21, H 4.55; found C 69.97, H 4.52.

2-Oxo-3-(triphenylphosphoranylidene)propanoic acid (**10**)

Method A: 1.74 g (5 mmol) of **9** were refluxed in 25 ml of 25% hydrochloric acid with stirring for 3 h. After evaporation of volatile components the resulting oil was dissolved in 20 ml of 1 M sodium hydroxide solution. The solution was extracted with dichloromethane (3 × 15 ml) to remove triphenylphosphine oxide. The product was precipitated by dropwise addition of 25% hydrochloric acid to the stirred and *ice*-cooled aqueous layer. The precipitate was collected, washed with cold water and recrystallized from 2-propanol to give colorless crystals, yield 1.10 g (63%), *m.p.* 218–219 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1} (OH), 1735 (COOH). – ^1H NMR: δ = 4.73 (d, J = 23.2 Hz, 1H, CH), 6.36 (br. s, 1H, OH), 7.59–7.74 (m, 15H, arom. H). – ^{13}C NMR: δ = 54.22 (dd, J = 8.2 Hz, CH), 124.51 (d, J = 91.3 Hz), 129.28 (dd, J = 12.3 Hz), 132.69 (dd, J = 10.5 Hz), 132.90 (dd, J = 2.6 Hz, arom. C), 165.70 (d, J = 19.0 Hz, C=O), 173.30 (s, COOH). – ^{31}P NMR: δ = 17.2. – MS (70 eV): *m/z* (%) = 348 (2) [M^+], 303 (100) [M^+ – COOH]. – $C_{21}H_{17}O_3P$ (348.3): calcd. C 72.41, H 4.92; found C 72.39, H 5.06.

Method B: A solution of 1.88 g (5 mmol) of 2-oxo-3-(triphenylphoshoranylidene)propanoic acid ethyl ester (**11**) [11] in 10 ml of methanol and 10 ml of 1 M sodium hydroxide solution was allowed to stand at room temperature for 5 d. After addition of 20 ml of water the mixture was extracted with dichloromethane (3 × 15 ml). The product was precipitated by dropwise addition of 25% hydrochloric acid to the stirred and ice-cooled aqueous layer. The precipitate was collected, washed with cold water and recrystallized from 2-propanol. Analytical data were in agreement with those reported under method A.

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