# Novel Iminium Compounds from *N*-Alkylanilinium Perchlorates and Aldehydes and Their Unexpected (Domino Type) Reactions

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*Received November 3, 1994*

Our investigations into the chemistry of preformed iminium salts[1] have led us to look for appropriate iminium systems with an aliphatic or aromatic fragment substituted for one of the H atoms adjacent to the iminium carbon. We describe here the results of our attempts to produce highly reactive iminium perchlorates, which are formed in the reaction between *N*-alkylanilinium perchlorates **1** and aliphatic or aromatic aldehydes **2**. Surprisingly, a new and unexpected (one pot; domino type[2]) reaction sequence is initiated if the parent aldehyde is unbranched at the α-position. This reaction sequence is started by the formation of an iminium salt **3**, followed by a Mannich reaction and an intramolecular Friedel–Crafts type ring closure. Finally, elimination of water and oxidative aromatization yields quinolinium salts **4**, **8**.

Preformed iminium salts are of great theoretical and practical interest.[3] Nevertheless, there are only few examples in the literature concerning the synthesis and application of compounds possessing carbon fragments other than methylene.[4] We were interested in the parameters that influence the reactivity of the iminium system, namely the effect of anion and steric and electronic effects of the substituents on the nitrogen and carbon atom. We chose to study the iminium perchlorates[4b] first because of their relative ease of availability.

Starting with dimethylamine hydroperchlorate we were able to derive a number of both aliphatic and aromatic substituted *N,N*-dimethyliminium perchlorates. This type of iminium salt is able to aminoalkylate ketones under relatively drastic conditions (DMF, 140 °C).[5] In this case the corresponding Mannich bases were not isolated but reacted further *in situ* to yield substituted quino-1,8- and quino-1,10-phenanthrolines.

Nevertheless, there is no procedure described in the literature to utilize such ternary iminium perchlorates specifically for aminoalkylations of carbonyl compounds. Our own experiences have shown that the reaction conditions known for the methylene iminium halides[6] do not succeed (electronic and/or steric effects). Unlike the simple carbonyl compounds, the more nucleophilic enamines do react with aromatic as well as with aliphatic substituted iminium salts (chlorides, tetrachloroaluminates, perchlorates, derived from dimethylamine and piperidine, respectively) even at low temperature (−85 °C).[7]

To enhance the reactivity of the ternary iminium perchlorates toward simple carbonyl compounds our idea was to exchange the strongly basic dimethylamine by the poorly basic *N*-methylaniline.[4c,8] This substitution should increase the carbonium ion character of the iminium carbon due to the diminished ability of the nitrogen to contribute its lone pair to the C–N bond.

Following the procedure described by Leonard and coworkers[4b,c] iminium perchlorates are formed in a simple condensation reaction by refluxing an appropriate secondary amine hydroperchlorate salt and an aldehyde or ketone in a solvent such as chloroform or 1,2-dichloroethane, the reaction water being removed by utilizing a Dean–Stark trap or a Soxhlet apparatus equipped with a desiccant such as molecular sieves or phosphorus pentoxide. Thus, refluxing a mixture of 1.0 equiv of *N*-methylaniline perchlorate (**1a**) (colorless plates, mp 79 °C, yield 74%)[4c] and 1.2 equiv of 4-(dimethylamino)-benzaldehyde (**2a**) in anhydrous chloroform in the presence of a catalytic amount of DBU produced the corresponding iminium system **3a** as bright yellow crystals in a nearly quantitative yield. According to the substitution pattern of the C=N$^+$ double bond, the isolated material consists of two isomers (*E*/*Z*), which were found to be present in the ratio of 1:4. NOESY experiments showed that the double bond of the main isomer is *Z*-configured (Scheme 1).

Our attempts to use this iminium salt **3a** as an aminoalkylating reagent for simple carbonyl compounds have not yet been successful. Cyclohexanone, as our standard ketone, did not react regardless of the solvent used (ether, THF, dichloromethane, chloroform, acetonitrile, DMF, and mixtures thereof) and whether the reaction was carried out at 20 °C or 130 °C. This behavior, together with the fact that the 4-(dimethylamino)benzylidene iminium salts exclusively show an intense color, might indicate that these compounds have to be regarded as phenylogous amidinium salts rather than simple iminium salts, with a lowered nucleophilicity due to the strong stabilizing effect of the ringbound amino group.

Replacement of 4-(dimethylamino)benzaldehyde by isobutyraldehyde (**2b**) resulted in the formation of the

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(1) (a) Westerwelle, U.; Esser, A.; Risch, N. *Chem. Ber.* **1991**, *124*, 571–576. (b) Risch, N.; Esser, A. *Synthesis* **1988**, 337–339. (c) Risch, N.; Esser, A. *Liebigs Ann. Chem.* **1992**, 233–237.

(2) Tietze, L. F.; Beifuss, U. *Angew. Chem.* **1993**, *105*, 137–170.

(3) For the most recent review see: Böhme, H.; Viehe, H. G. Iminium Salts in Organic Chemistry Part 1, In *Advances in Organic Chemistry*; John Wiley & Sons., Inc.: New York, 1976; Vol. 9, Chapters 1–3.

(4) The older literature is covered in: (a) Paukstelis, J. V. In *Enamines: Synthesis, Structure, and Reactions*; Cook, A. G., Ed.; M. Dekker: New York, 1969; Vol. 5, pp 169–209. See also: (b) Leonard, N. J.; Paukstelis, J. V. *J. Org. Chem.* **1963**, *28*, 3021–3024. (c) Leonard, N. J.; Klainer, J. A. *J. Heterocycl. Chem.* **1971**, *8*, 215–219. (d) Dean, R. T.; Padgett, H. C.; Rapoport, H. *J. Am. Chem. Soc.* **1976**, *98*, 7448–7449. (e) Lamchen, M.; Pugh, W.; Stephen, A. M. *J. Chem. Soc.* **1954**, 4418–4425. (f) Damico, R.; Broaddus, C. D. *J. Org. Chem.* **1966**, *31*, 1607–1612. (g) Gross, H.; Gloede, J.; Freiberg, J. *Liebigs Ann. Chem.* **1967**, *702*, 68–74. (h) Ohwada, T.; Yamagata, N.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 1364–1373. (i) Childs, R. F.; Dickie, B. D. *J. Am. Chem. Soc.* **1983**, *105*, 5041–5046. (j) Libman, N. M. *J. Org. Chem. USSR* **1967**, *3*, 1196–1199.

(5) Westerwelle, U.; Risch, N. *Tetrahedron Lett.* **1993**, *34*, 1775–1778.

(6) For examples see: (a) Kinast, G.; Tietze, L. F. *Angew. Chem.* **1976**, *88*, 261–262. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 239. (b) Schreiber, J.; Maag, H.; Hashimoto, N.; Eschenmoser, A. *Angew. Chem.* **1971**, *83*, 355–357. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 330. (c) Jasor, Y.; Gaudry, M.; Luche, M. J.; Marquet, A. *Tetrahedron* **1977**, *33*, 295–303. (d) Volz, H.; Kiltz, H.-H. *Liebigs Ann. Chem.* **1971**, *752*, 86–101. (e) Esser, A. Dissertation, Universität Bielefeld, 1989. (f) Beugelmans, R.; Benadjila-Iguertsira, L.; Negron, G.; Roussi, G. *Can. J. Chem.* **1985**, *63*, 725–734.

(7) Risch, N.; Arend, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2422–2423.

(8) See also: (a) Böhme, H.; Eichler, D. *Chem. Ber.* **1967**, *100*, 2131–2137. (b) Volz, H.; Kiltz, H.-H. *Liebigs Ann. Chem.* **1971**, *752*, 86–101.

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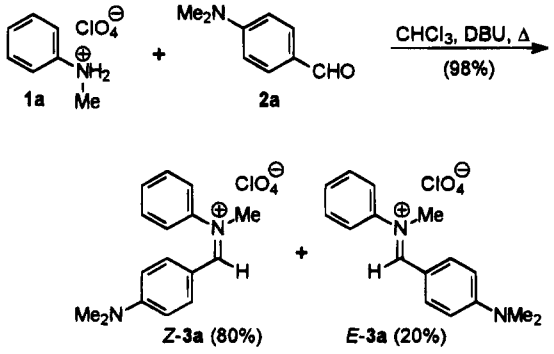
**Scheme 1**




expected *N*-methyl-*N*-phenylisobutylidene iminium perchlorate **3b** (colorless crystals, 63% yield). Again, a mixture of the *Z*- and *E*-form was isolated in the ratio of 4:1. In contrast to the aromatic substituted representative, this compound is very sensitive to moisture; the NMR sample reverted to the starting materials after standing for 15 min.

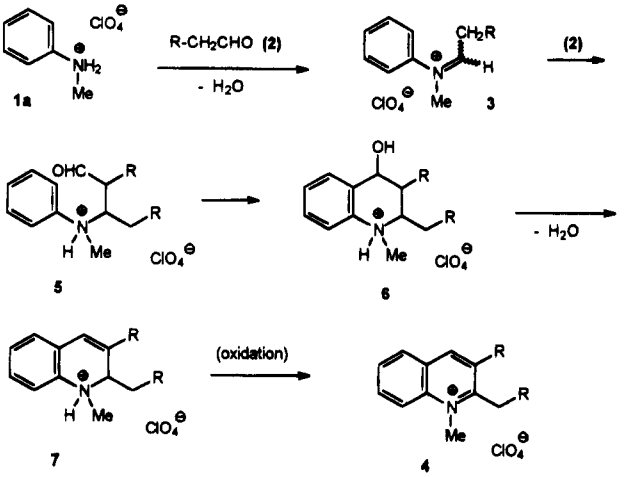
Following the procedure described above with isovaleraldehyde (**2c**) in place of isobutyraldehyde we isolated surprisingly only a small number of colorless crystals. The $^1$H NMR spectrum of this product did not give the responses expected for an iminium salt. In particular, the absence of the multiplet of the proton adjacent to the C=N$^+$ bond (normally in the region 8.2–9.2 ppm), combined with the appearance of two singlets at 4.6 and 8.8 ppm and two doublets at 1.1 and 1.4 ppm, indicated that the reaction did not stop at the iminium level. From additional spectroscopic analysis we were able to assign structure **4c** to the isolated material.[9]

In order to explain this result we propose the following domino type reaction mechanism (Scheme 2).[13] The first step of the sequence is the generation of the iminium perchlorate **3** in the expected manner. The reaction cascade is then continued by the aminoalkylation of excess of the aldehyde, producing the intermediate **5**. This compound (or rather its unprotonated form, which exists in equilibrium with **5**) undergoes an intramolecular cyclization in the sense of an electrophilic aromatic substitution of the electron rich aniline moiety, leading to the tetrahydroquinoline system **6**. This intermediate eliminates water forming **7** with a new double bond conjugated to the aromatic system. The final oxidation step produces the aromatic quinolinium system **4**.

According to this mechanism, the complete sequence of reaction steps can only take place if the parent aldehyde possesses an α-methylene group. Thus, with aromatic aldehydes and aliphatic aldehydes branched in the α-position the expected iminium salts can be isolated as shown above for **2a**,**b**. In contrast, other unbranched aliphatic (and araliphatic) aldehydes produce the corresponding quinolinium systems **4**. Some examples are shown in Scheme 2.

Because of the modest yields obtained at the beginning (12–22%), we intensified our investigations in order to optimize the reaction conditions. Nevertheless, the reaction seems to be influenced neither by solvent effects (yields are in the same range whichever solvent is used: chloroform, dichloromethane, toluene, DMF, acetonitrile) nor by temperature (room temperature or boiling temperature of the chosen solvent, respectively). Increasing the excess of aldehyde (up to a ratio of 5:1 with regard to the amount of amine hydroperchlorate) does not significantly improve the yields of the quinolinium compounds, nor does the presence of an oxidizing agent (cuprous acetate,[10] or oxygen by bubbling air through the reaction mixture). On the other hand, the presence of Lewis acids (in catalytic amounts), especially aluminum chloride, results in a decrease in the number of side reactions and a slight improvement in the yields. Thus, especially in the case of the smaller unbranched aliphatic aldehydes, yields of up to 44% are attained.

**Scheme 2**




| R-CH$_2$CHO | | Perchlorate | Quinolinium Salts (Yield) |
|---|---|---|---|
| R = | | | |
| $CH_3$ | **2c** | **1a** | **4c** (45%) |
| $CH_3CH_2$ | **2d** | **1a** | **4d** (15%) |
| $CH_3(CH_2)_2$ | **2e** | **1a** | **4e** (28%) |
| $(CH_3)_2CH$ | **2f** | **1a** | **4f** (13%) |
| $CH_3(CH_2)_4$ | **2g** | **1a** | **4g** (23%) |
| $CH_3(CH_2)_6$ | **2h** | **1a** | **4h** (30%) |
| $C_6H_5CH_2$ | **2i** | **1a** | **4i** (5%) |
| $CH_3CH_2$ | **2d** | **1b** | **4k** (23%) |
| $CH_3CH_2$ | **2d** | **1c** | **4m** (17%) |

**1b**: N-ethylanilinium perchlorate; **1c**: N-benzylanilinium perchlorate

The exchange of the anion in the amine salt ($Cl^-$, $CF_3CO_2^-$) leads to the failure of the reaction. This might be due to the generally much higher tendency of perchlorate salts to crystallize, compared with salts which possess other anions.

Despite the fact that in a few cases the yields are yet only modest, this remarkable new reaction normally comprises a very simple and efficient access to *N*-alkylquinolinium compounds. Starting with the appropriate amine component, even tricyclic quinolinium salts, such as the benzo-fused quinolizidinium compounds **8a** and **8b**, are produced (Scheme 3). This reaction might be used as a simple entrance to the synthesis of lycopodium type alkaloids. Apart from this special aim, this type of quinoline derivative is of current interest e.g. as a NADPH model compound,[11] as a structural subunit in certain antibiotics,[12] as well as in the creation of dyestuffs.

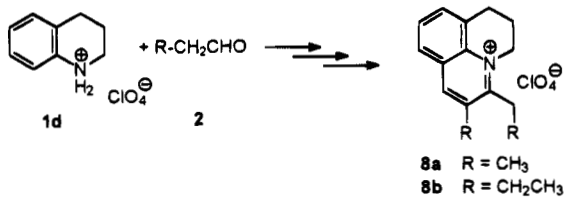
(9) All new compounds were characterized by NMR, IR, and mass spectral data and by elemental analysis. See supplementary material.

(10) Bell, T. W.; Rothenberger, S. D. *Tetrahedron Lett.* **1987**, *28*, 4817–4820.

(11) Ohno, A.; Mikata, Y.; Goto, M.; Kashiwagi, T.; Tanaka, T.; Sawada, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 81–86.

(12) Christensen, B. G.; Johnston, D. B. R.; Schmitt, S. M. Merck and Co., Inc. Eur. Pat. Appl. EP 170073, Feb 5, 1986; *Chem. Abstr.* *107*(25): 236355y.

**Scheme 3**




In summary, we have demonstrated that the tuning of the reactivity of iminium perchlorates may be achieved by the choice of a weakly basic aromatic amine component. Condensation of *N*-methylaniline hydroperchlorate and other secondary aromatic amine hydroperchlorate salts with aldehydes results in the formation of iminium perchlorates. These compounds are isolable if the parent aldehyde possesses no more than one proton in the α-position. Iminium salts derived from α-methylene aldehydes immediately aminoalkylate surplus aldehyde, thus initiating a domino type reaction which produces substituted *N*-alkylquinolinium perchlorates, the substitution pattern being determined by the aldehyde used. In order to achieve a more flexible substitution pattern, we are currently investigating possibilities of decoupling the reaction cascade.

## Experimental Section

Melting points were uncorrected. Chemical shifts are reported in ppm relative to $Me_4Si$. An asterisk (*) designates the main isomer. All mass spectra were recorded by employing the FAB/SIMS technique. Standard conditions: CsI, voltage of acceleration 30 keV, voltage of ion acceleration 8 keV. Matrix unless otherwise stated: glycerine/trifluoroacetic acid. Perchloric acid (70%), the aromatic amines, and the aldehydes were purchased from Merck. The amines as well as the aldehydes had been distilled prior to use. Chloroform was distilled from $CaH_2$; THF was distilled from potassium directly before use. **Perchloric acid and larger amounts of crystalline perchlorate salts especially should be handled with care. All operations including the removal of solvent and the drying in vacuo should be performed below 50 °C.**

**General Procedure for the Synthesis of *N*-Alkylaniline Hydroperchlorates (1a–c) and 1,2,3,4-Tetrahydroquinoline Hydroperchlorate (1d).** In a round bottom flask 0.5 mol of freshly distilled amine was cooled to 0 °C. Under stirring, a solution of 0.5 mol of perchloric acid (aqueous solution, 70% by weight) in ethanol 1:1 v/v was added dropwise. Stirring was continued for an additional 1 h at 0 °C, and then the pH value was measured and corrected to 4–5 by the dropwise addition of amine. The solvent was evaporated and the residue was dried in vacuo. The crude crystalline product was dissolved in a mixture of dichloromethane and isopropyl alcohol (3:1 v/v) and was precipitated by the addition of a mixture of heptane and ether (1:1 v/v). Crystallization from dichloromethane provided the analytically pure material.

***N*-Methylaniline hydroperchlorate (1a)**:[4c] from 53.5 g of *N*-methylaniline and 70.9 g of perchloric acid, yield 74%; mp 79 °C (colorless prisms); $^1$H NMR (200 MHz, $CDCl_3$, TMS) δ 7.52 (s, 5 H), 3.29 (s, 3 H).

***N*-Ethylaniline hydroperchlorate (1b)**: from 60.7 g of *N*-ethylaniline and 70.9 g of perchloric acid, yield 95%; mp 62 °C (pale yellow crystals); $^1$H NMR (80 MHz, $CDCl_3$, TMS) δ 7.77 (s, 2 H), 7.39 ("s", 5 H), 3.50 (q, $^3J$ = 7.3 Hz, 2 H), 1.36 (t, $^3J$ = 7.3 Hz, 3 H).

***N*-Phenylbenzylamine hydroperchlorate (1c)**: from 3 g of *N*-benzylaniline and 2.3 g of perchloric acid, yield 65%; mp 112 °C (colorless prisms); $^1$H NMR (200 MHz, $CDCl_3$, TMS) δ 9.36 (s, 2H), 7.39–7.20 (m, 10H), 4.63 (s, 2H).

**1,2,3,4-Tetrahydroquinoline hydroperchlorate (1d)**: from 66.5 g of 1,2,3,4-tetrahydroquinoline and 70.9 g of perchloric acid, yield 76%; mp 137 °C (colorless needles); IR (KBr) 3181, 3007, 2907, 2812, 2721, 2644, 2474, 1552, 1460, 1093, 991, 956, 937, 906, 835, 752, 626, 432 cm$^{-1}$; $^1$H NMR (300 MHz, $CD_3CN$) δ 8.51 (s, 2 H), 7.46–7.32 (m, 4 H), 3.55 (m, 2 H), 2.91 (t, $J$ = 6.5 Hz, 2H), 2.13 (m, 2 H); $^{13}$C NMR (75 MHz, $CD_3CN$) δ 132.1, 131.0, 129.7, 129.2, 127.5, 123.5, 43.5, 24.2, 19.0. Anal. Calcd for $C_9H_{12}ClNO_4$: C, 46.27; H, 5.18; N, 5.99. Found: C, 46.15; H, 5.36; N, 6.18.

**General Procedure for the Synthesis of Iminium Salts 3 and Quinolinium Salts 4, 8.** A mixture of 13 mmol of *N*-alkylaniline hydroperchlorate **1** and 16 mmol of the respective aldehyde **2** in 30 mL of dry chloroform in the presence of catalytic amounts of DBU and aluminum chloride was refluxed for 14 h in a microsoxhlet apparatus equipped with molecular sieves, 3 Å (argon atmosphere). The solvent was removed from the deeply colored solution under reduced pressure, and the residual viscous oil was dissolved in dry THF. On cooling, the crystalline product precipitated from the solution, yielding iminium compounds **3** or quinolinium compounds **4, 8** depending on whether the parent aldehyde had or had not been branched in the α-position.

**4-(Dimethylamino)benzylidene-*N*-methylanilinium perchlorate (3a)**: from 2.70 g of **1a** and 2.39 g of 4-(dimethylamino)benzaldehyde (**2a**), yield 98%, mixture of *Z*- and *E*-isomers, ratio 4:1; mp 180 °C (yellow needles, from acetonitrile/diethyl ether); IR (KBr) 3050, 2920, 1595, 1570, 1530, 1380, 1200, 1190, 1175, 1085, 830, 775, 695, 620 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$/$CD_3CN$ (20:1), TMS) δ 8.61*/8.25 ($m_c$, 1 H), 7.74–7.42 (m, 5 H), 7.98/7.06* (m, 2 H), 6.94/6.53* (m, 2 H), 4.14/3.98* ("s", 3 H), 3.27/3.13* (s, 6 H); $^{13}$C NMR (63 MHz, $CD_3CN$, TMS) δ 166.0*/164.2, 157.0/156.8*, 147.6/142.5*, 138.9*/137.8, 132.0*/130.7, 131.4*/130.1, 125.1*/123.7, 114.4/113.2*, 113.4/112.9*, 52.2*/44.7, 40.7/40.5*. Anal. Calcd for $C_{16}H_{19}ClN_2O_4$: C, 56.72; H, 5.65; N, 8.27. Found: C, 56.99; H, 5.77; N, 8.19.

**Isobutylidene-*N*-methylanilinium perchlorate (3b)**: from 2.70 g of **1a** and 1.16 g isobutyraldehyde (**2b**), yield 63%, mixture of *Z*- and *E*-isomers, ratio 5:1; mp 112–117 °C; $^1$H NMR (250 MHz, $CDCl_3$/$CD_3CN$ (20:1), TMS) δ 8.65*/8.35 ($m_c$, 1 H), 7.63–7.45 (m, 5 H), 4.08 (d, $J$ = 1.1 Hz, 3 H), 2.61–2.41 (m, 1 H), 1.47/1.28* (d, $J$ = 6.7 Hz, 6 H). Anal. Calcd for $C_{11}H_{16}ClNO_4$: C, 50.49; H, 6.16; N, 5.35. Found: C, 51.33; H, 6.77; N, 4.92.

**2-Ethyl-1,3-dimethylquinolinium perchlorate (4c)**: from 2.70 g of **1a** and 0.93 g of **2c**, yield 45%; mp 92 °C (colorless crystals); IR (KBr) 3005, 2974, 2658, 2436, 1649, 1508, 1452, 1379, 1238, 1089, 974, 779, 696, 625 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$/$CD_3OD$ (10:1), TMS) δ 8.79 (s, 1 H), 8.39 (d, $J$ = 9.0 Hz, 1 H), 8.17 (d, $J$ = 8.1 Hz, 1 H), 8.13 (t, $J$ = 8.8 Hz, 1 H), 7.91 (t, $J$ = 7.6 Hz, 1 H), 4.55 (s, 3 H), 3.47 (q, $J$ = 7.7 Hz, 2 H), 2.75 (s, 3 H), 1.48 (t, $J$ = 7.7 Hz, 3 H); $^{13}$C NMR (75 MHz, $CDCl_3$/$CD_3OD$ (10:1), TMS) δ 163.9, 146.0, 138.4, 134.5, 132.1, 129.4, 129.2, 127.6, 118.0, 39.2, 23.3, 19.1, 10.5; MS (FAB) *m/z* (rel intensity) 186 (50, $C_{13}H_{16}N^+$), 153 (22), 148 (100).

**3-Ethyl-1-methyl-2-propylquinolinium perchlorate (4d)**: from 2.70 g of **1a** and 1.15 g of **2d**, yield 15%; mp 148 °C (light yellow crystals, from THF); IR (KBr) 3130, 3110, 3070, 3050, 2970, 2930, 2875, 1615, 1595, 1505, 1450, 1375, 1230, 1085, 780, 765, 620 cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$/$CD_3CN$ (20:1), TMS) δ 8.66 (s, 1 H), 8.35 ($m_c$, 1 H), 8.15–8.05 (m, 2 H), 7.85 ($m_c$, 1 H), 4.62 (s, 3 H), 3.38 ($m_c$, 2 H), 3.02 (q, $J$ = 7.5 Hz, 2 H), 1.85–1.75 (m, 2 H), 1.46 (t, $J$ = 7.5 Hz, 3 H), 1.22 (t, $J$ = 7.3 Hz, 3 H); $^{13}$C NMR (63 MHz, $CDCl_3$/$CD_3CN$ (20:1), TMS) δ 163.1, 144.3, 138.7, 137.8, 135.0, 129.9, 129.6, 128.0, 118.8, 40.4, 33.3, 25.9, 21.7, 14.4, 14.0; MS (FAB) *m/z* (rel intensity) 214 (100, $C_{15}H_{20}N^+$). Anal. Calcd for $C_{15}H_{20}ClNO_4$: C, 57.42; H, 6.43; N, 4.46. Found: C, 57.47; H, 6.44; N, 4.43.

**2-Butyl-1-methyl-3-propylquinolinium perchlorate (4e)**: from 2.70 g of **1a** and 1.35 g of **2e**, yield 28%; mp 154 °C (colorless crystals); IR (KBr) 3011, 2930, 2864, 1650, 1601, 1487, 1368, 1093, 781, 638, 625, 407 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$, TMS) δ 8.70 (s, 1 H), 8.38 (d, $J$ = 9.0 Hz, 1 H), 8.13 (d, $J$ = 8.1 Hz, 1 H), 8.07 (t, $J$ = 7.3 Hz, 1 H), 7.83 (t, $J$ = 7.2 Hz, 1 H), 4.62 (s, 3 H), 3.34 (t, $J$ = 8.1 Hz, 2H), 2.91 (t, $J$ = 7.8 Hz, 2 H), 1.93–1.50 (m, 6 H), 1.11 (t, 3 H), 1.06 (t, 3 H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 163.5, 145.8, 139.2, 136.9, 135.5, 130.4, 129.9, 128.4, 119.1, 40.7, 35.2, 31.7, 30.4, 23.7, 23.4, 14.3, 13.9. Anal. Calcd for $C_{21}H_{34}ClNO_4$: C, 63.06; H, 8.57; N, 3.50. Found: C, 62.88; H, 9.00; N, 3.42.

(13) The proposed mechanistic pathway is still speculative. For example, a Diels–Alder reaction between **3** and the enolic form of the aldehyde can also be discussed.

**2-Isobutyl-3-isopropyl-1-methylquinolinium perchlorate (4f)**: from 2.70 g of **1a** and 1.38 g of **2f**, yield 13%; mp 179 °C (colorless needles, from THF); IR (KBr) 3140, 3110, 3070, 2970, 2935, 2880, 1620, 1600, 1505, 1460, 1450, 1385, 1370, 1360, 1230, 1165, 1090, 780, 760, 620 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 8.78 (s, 1 H), 8.36 ($m_c$, 1 H), 8.19 ($m_c$, 1 H), 8.07 ($m_c$, 1 H), 7.83 ($m_c$, 1 H), 4.63 (s, 3 H), 3.50–3.38 (m, 3 H), 2.19 (sept, $J$ = 6.6 Hz, 1 H), 1.43 (d, $J$ = 6.8 Hz, 6 H), 1.08 (d, $J$ = 6.6 Hz, 6 H); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS) $\delta$ 161.8, 143.5, 142.8, 138.9, 135.3, 130.2, 129.6, 128.2, 118.8, 41.3, 38.6, 30.4, 29.9, 23.5, 22.4; MS (FAB), *m/z* (rel intensity) = 242 (100, $C_{17}H_{24}N^+$). Anal. Calcd for $C_{17}H_{24}ClNO_4$: C, 59.73; H, 7.08; N, 4.10. Found: C, 59.26; H, 7.19; N, 4.06.

**2-Hexyl-1-methyl-3-pentylquinolinium perchlorate (4g)**: from 2.70 g of **1a** and 1.83 g of **2g**, yield 23%; mp 117 °C (colorless crystals); IR (KBr) 3021, 2928, 2858, 1647, 1599, 1512, 1456, 1381, 1236, 1093, 943, 779, 637, 625 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 8.67 (s, 1 H), 8.37 (d, $J$ = 9.0 Hz, 1 H), 8.15 (d, $J$ = 8.1 Hz, 1 H), 8.06 (t, $J$ = 7.3 Hz, 1 H), 7.83 (t, $J$ = 7.5 Hz, 1 H), 4.61 (s, 3 H), 3.37 (t, $J$ = 8.1 Hz, 2 H), 2.94 (t, $J$ = 7.9 Hz, 2 H), 1.75 (m, 4 H), 1.60 (m, 2 H), 1.37 (m, 8 H), 0.94 (t, 3 H), 0.92 (t, 3 H); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS) $\delta$ 162.9, 145.1, 138.7, 136.6, 134.9, 129.8, 129.4, 127.8, 118.6, 40.2, 32.7, 31.5, 31.4, 31.1, 29.7, 29.4, 28.0, 22.3, 22.2, 13.9; MS (FAB) *m/z* (rel intensity) 298 (100, $C_{21}H_{34}N^+$), 254 (25), 240 (27), 234 (28). Anal. Calcd for $C_{21}H_{34}ClNO_4$: C, 63.06; H, 8.57; N, 3.50. Found: C, 62.88; H, 9.00; N, 3.42.

**3-Heptyl-1-methyl-2-octylquinolinium perchlorate (4h)**: from 2.70 g of **1a** and 2.28 g of **2h**, yield 30%; mp 117 °C (colorless crystals); $^1H$ NMR (200 MHz, $CDCl_3$, TMS) $\delta$ 8.66 (s, 1 H), 8.42 (m, 1 H), 8.11 (m, 2 H), 7.83 ($m_c$, 1 H), 4.65 (s, 3 H), 3.41 (t, $J$ = 8.1 Hz, 2 H), 2.95 (t, $J$ = 7.9 Hz, 2 H), 1.85–1.20 (m, 24 H), 0.93 ($m_c$, 6 H); $^{13}C$ NMR (50 MHz, $CDCl_3$, TMS) $\delta$ 163.6, 145.4, 139.3, 137.2, 135.5, 130.2, 130.0, 128.3, 119.3, 40.8, 33.3, 32.1, 30.5, 30.3, 29.8, 29.5, 29.4, 28.6, 23.0, 14.5. Anal. Calcd for $C_{25}H_{40}ClNO_4$: C, 66.13; H, 8.88; N, 3.08. Found: C, 66.25; H, 8.73; N, 2.96.

**3-Benzyl-1-methyl-2-(2-phenylethyl)quinolinium perchlorate (4i)**: from 2.70 g of **1a** and 2.15 g of **2i**, yield 5%; mp 188 °C (light yellow crystals); IR (KBr) 3005, 2978, 1601, 1510, 1452, 1385, 1169, 1093, 750, 700, 623, 580, 492 $cm^{-1}$; $^1H$ NMR (200 MHz, $CD_3CN$, TMS) $\delta$ 8.77 (s, 1 H), 8.44 (d, $J$ = 8.8 Hz, 1 H), 8.22 (m, 2 H), 7.99 (m, 1 H), 7.46–7.22 (m, 10 H), 4.56 (s, 3 H), 4.33 (s, 2 H), 3.62 (m, 2 H), 2.97 (m, 2 H); $^{13}C$ NMR (50 MHz, $CD_3CN$, TMS) $\delta$ 162.8, 147.2, 139.7, 139.5, 138.0, 135.9, 135.4, 130.5, 130.1, 129.5, 129.4, 129.2, 128.9, 128.4, 127.6, 127.4, 119.3, 40.8, 38.9, 33.9, 33.1; MS (FAB) *m/z* (rel intensity) 338 (100, $C_{25}H_{24}N^+$), 246 (52), 232 (24), 217 (13). Anal. Calcd for $C_{25}H_{24}ClNO_4$: C, 68.57; H, 5.52; N, 3.20. Found: C, 68.43; H, 5.47; N, 3.11.

**1,3-Diethyl-2-propylquinolinium perchlorate (4k)**: from 2.88 g of **1b** and 1.15 g of **2d**, yield 23%; mp 168 °C (colorless needles, from THF); IR (KBr) 3135, 3060, 3040, 2970, 2940, 2875, 1620, 1600, 1500, 1470, 1435, 1375, 1365, 1340, 1160, 1085, 775, 755, 620 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3/CD_3CN$ (20:1), TMS) $\delta$ 8.70 (s, 1 H), 8.36 ($m_c$, 1 H), 8.18–8.07 (m, 2 H), 7.84 ($m_c$, 1 H), 5.10 (q, $J$ = 7.3 Hz, 2 H), 3.29 ($m_c$, 2 H), 3.03 (q, $J$ = 7.4 Hz, 2 H), 1.92–1.76 (m, 2 H), 1.75 (t, $J$ = 7.3 Hz, 3 H), 1.48 (t, $J$ = 7.4 Hz, 3 H), 1.25 (t, $J$ = 7.3 Hz, 3 H); $^{13}C$ NMR (63 MHz, $CDCl_3/CD_3CN$ (20:1), TMS) $\delta$ 162.0 (C-2), 144.5 (C-4), 138.0, 137.4, 135.2, 130.3, 129.5, 128.6, 118.8, 48.1 (1-$CH_2$), 33.1 (2-$CH_2$), 25.4, 22.3, 15.1, 14.7, 14.0; MS (FAB) *m/z* (rel intensity) = 228 (100, $C_{16}H_{22}N^+$). Anal. Calcd for $C_{16}H_{22}ClNO_4$: C, 58.63; H, 6.77; N, 4.27. Found: C, 58.86; H, 6.75; N, 4.20.

**1-Benzyl-3-ethyl-2-propylchinolinium perchlorate (4m)**: from 3.69 g of **1c** and 1.15 g of **2d**, yield 17%; mp 212 °C (light yellow crystals); $^1H$ NMR (200 MHz, $CDCl_3/CD_3OD$ (5:1), TMS) $\delta$ 8.88 (s, 1 H), 8.23 ($m_c$, 1 H), 8.12 ($m_c$, 1 H), 8.09–7.85 (m, 2 H), 7.38 (m, 5 H), 3.85 (s, 2 H), 3.29 (m, 2 H), 3.11 (q, $J$ = 7.4 Hz, 2 H), 1.82 (m, 2 H), 1.55 (t, $J$ = 7.4 Hz, 3 H), 1.17 (t, $J$ = 7.3 Hz, 3 H). Anal. Calcd for $C_{21}H_{24}ClNO_4$: C, 64.69; H, 6.20; N, 3.59. Found: C, 64.53; H, 6.09; N, 3.70.

**5-Ethyl-6-methyl-2,3-dihydro-1*H*-benzo[*ij*]quinolizinium perchlorate (8a)**: from 3.04 g of **1d** and 0.93 g of **2c**, yield 15%; mp 129 °C (colorless crystals); $^1H$ NMR (300 MHz, $CDCl_3/CD_3OD$ (10:1), TMS) $\delta$ 8.69 (s, 1 H), 7.89 ($m_c$, 1 H), 7.78 ($m_c$, 2 H), 4.93 (t, $J$ = 5.7 Hz, 2 H), 3.45–3.36 (m, 4 H), 2.72 (s, 3 H), 2.49 (m, 2 H), 1.45 (t, $J$ = 7.4 Hz, 3 H), 1.21 (t, $J$ = 7.3 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS) $\delta$ 167.4, 150.3, 136.4, 134.2, 133.5, 132.0, 129.1, 127.4, 56.6, 31.1, 25.7, 15.1, 14.9. Anal. Calcd for $C_{15}H_{18}ClNO_4$: C, 57.79; H, 5.82; N, 4.49. Found: C, 58.11; H, 5.90; N, 4.63.

**6-Ethyl-5-propyl-2,3-dihydro-1*H*-benzo[*ij*]quinolizinium perchlorate (8b)**: from 3.04 g of **1d** and 1.15 g of **2d**, yield 24%; mp 125 °C (colorless crystals); IR (KBr) 3061, 2932, 2872, 1603, 1501, 1385, 1323, 1091, 767, 623 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, TMS) $\delta$ 8.61 (s, 1 H), 7.95 (d, $J$ = 7.8 Hz, 1 H), 7.74 (m, 2 H), 4.92 (t, $J$ = 5.4 Hz, 2 H), 3.33 (m, 2 H), 3.25 (t, $J$ = 6.1 Hz, 2 H), 2.97 (q, $J$ = 7.4 Hz, 2 H), 2.46 (m, 2 H), 1.77 (m, 2 H), 1.43 (t, $J$ = 7.4 Hz, 3 H), 1.20 (t, $J$ = 7.3 Hz, 3 H); $^{13}C$ NMR (75 MHz, $CDCl_3$, TMS) $\delta$ 161.6, 143.9, 137.3, 135.8, 133.0, 129.1, 128.8, 127.6, 52.3, 32.4, 26.7, 25.4, 21.2, 21.1, 14.2, 13.8; MS (FAB) *m/z* (rel intensity) 240 (91, $C_{17}H_{22}N^+$), 190 (12), 186 (56), 153 (39). Anal. Calcd for $C_{17}H_{22}ClNO_4$: C, 60.09; H, 6.53; N, 4.12. Found: C, 59.93; H, 6.46; N, 4.03.

**Acknowledgment.** We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their financial support.

JO941845U