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# Synthesis and Properties of Cadmium-containing Quinolinium and Pyrilium Salts

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**Abstract**—Consecutive treatment of methyl-substituted quinolinium and 2,6-diarylpyrilium perchlorates with sodium ethylate and equimolar amount of anhydrous cadmium(II) trifluoroacetate gives 2- and 4-methylenecadmium-containing salts of the above heterocyclic cations in 80–97% yields. The reactions of the cadmium-containing quinolinium and pyrilium salts with hydrochloric acid, acetic anhydride, mercuric trifluoroacetate, $SnCl_2$, and nickel(II) trifluoroacetate, resulting in substitution of the $CdOCOCF_3$ group by hydrogen, Ac, $HgOCOCF_3$, SnCl, and $NiOCOCF_3$, respectively, were studied.

Earlier we showed [1, 2] that pyrilium and quinolinium salts with active methyl groups in the 2 and 4 positions of the heterocyclic system are readily mercurated under the action of mercury salts by way of substitution methyl hydrogen atoms by HgX (X = $CH_3COO$, $CF_3COO$). We attempted to accomplish the same reactions with similar salts of cadmium which is an isoelectronic analog of mercury. However, under the “direct” mercuration conditions [1, 2] the above salts of heterocyclic cations failed to react with equimolar amounts of anhydrous cadmium acetate or trifluoroacetate under reflux in anhydrous ethanol. Therefore, for preparing cadmium-containing quinolinium and pyrilium salts, we used the “indirect” mercuration procedure [1, 2]. As a first step, quinolinium salts **I**–**V** or 2-methyl-4,6-bis(4-*p*-butoxyphenyl)pyrilium perchlorate (**VI**) were treated with equimolar amount of sodium ethylate to obtain brightly colored solutions of unstable methylene bases **VII**–**XII**. The sodium perchlorate was separated, and the filtrate containing compounds **VII**–**XII**, was treated with equimolar amount of anhydrous cadmium(II) acetate or trifluoroacetate. The reaction with cadmium(II) acetate almost did not occur at room temperature, while on heating methylene bases **VII**–**XII** decomposed to give reddish-brown tarry materials. In the second case, just after addition of cadmium(II) trifluoroacetate the color of the reaction mixture changed abruptly within 2–3 min at room temperature. After appropriate treatment of the reaction mixture we obtained cadmium-containing quinolinium and pyrilium trifluoroacetates (**XIII**–**XVII** and **XVIII**, respectively) (Table 1) in 80–97% yields. The products proved to be highly hygroscopic substances deliquescing in air in 10–15 min.

**Table 1.** Yields, constants, and elemental analyses of compounds **XIII–XVIII, XXVI**, and **XXVII**

| Comp. no. | Yield, % | mp, °C | Found, % | | | | Formula | Calculated, % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | Cd (Cl) | N | | C | H | Cd (Cl) | N |
| **XIII** | 97 | 90–92 | 36.36 | 2.22 | 22.69 | 2.83 | $C_{15}H_{11}CdF_6NO_4$ | 36.87 | 2.43 | 22.80 | 2.94 |
| **XIV** | 88 | 101–102 | 36.36 | 2.22 | 22.69 | 2.83 | $C_{15}H_{11}CdF_6NO_4$ | 36.71 | 2.54 | 22.68 | 2.74 |
| **XV** | 91 | 142–144 | 37.72 | 2.55 | 22.04 | 2.75 | $C_{16}H_{13}CdF_6NO_4$ | 37.85 | 2.68 | 21.93 | 2.81 |
| **XVI** | 93 | 136–137 | 43.09 | 2.33 | 20.16 | 2.51 | $C_{20}H_{13}CdF_6NO_4$ | 42.96 | 2.48 | 20.33 | 2.44 |
| **XVII** | 85 | 155–156 | 43.09 | 2.33 | 20.16 | 2.51 | $C_{20}H_{13}CdF_6NO_4$ | 43.21 | 2.56 | 20.28 | 2.64 |
| **XVIII** | 80 | 100–102 | 49.45 | 4.12 | 15.42 | – | $C_{30}H_{30}CdF_6O_7$ | 50.20 | 4.02 | 15.60 | – |
| **XXVI** | 35 | 160–162 | 47.09 | 3.35 | (17.18) | 3.57 | $C_{16}H_{13}Cl_2NSn$ | 46.98 | 3.18 | (17.37) | 3.43 |
| **XXVII** | 48 | 182–184[a] | 47.83 | 2.64 | – | 2.93 | $C_{20}H_{13}F_6NNiO_4$ | 47.65 | 2.58 | – | 2.78 |

[a] With decomposition.

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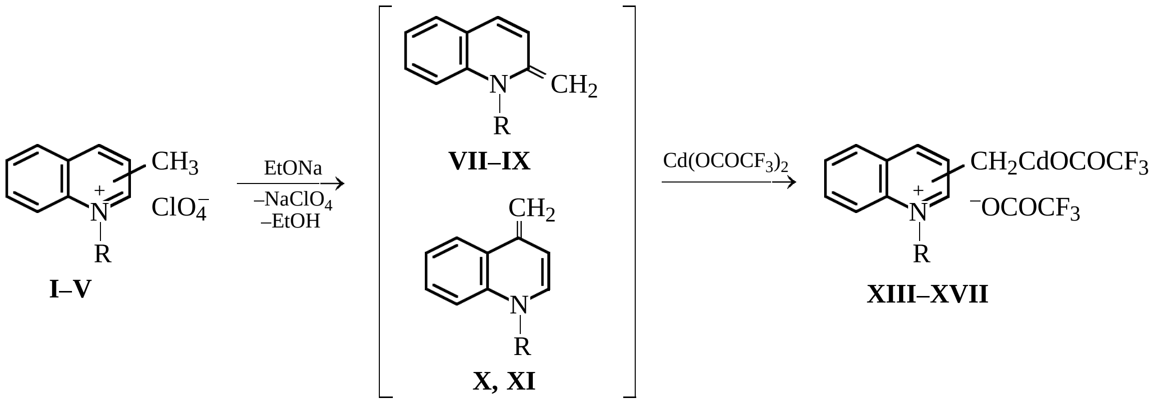
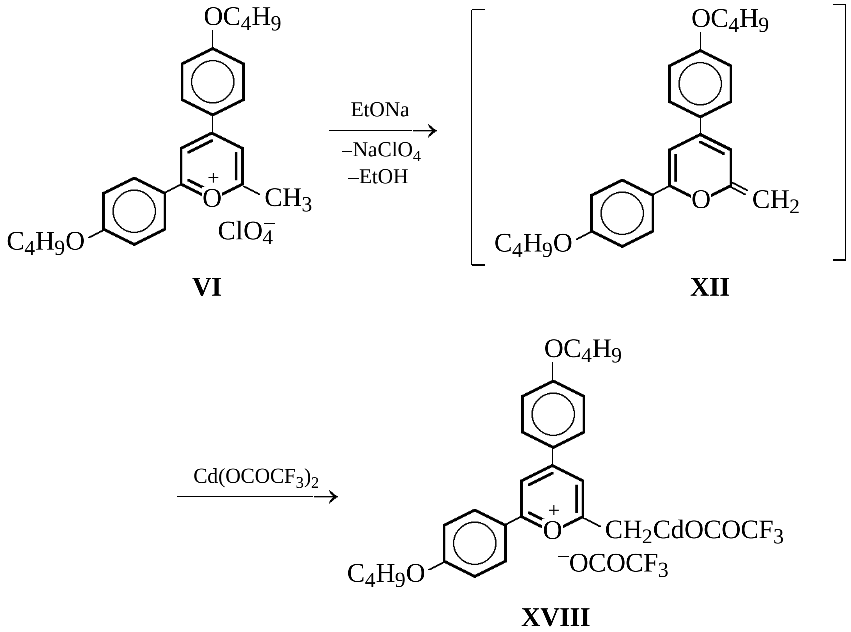
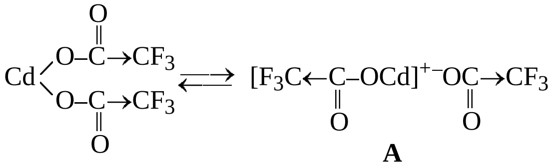


R = $CH_3$ (**I, II, VII, X, XIII, XIV**), $C_2H_5$ (**III, VIII, XV**), $C_6H_5$ (**IV, V, IX, XI, XVI, XVII**); 2-$CH_3$ (**I, III, IV**), 4-$CH_3$ (**II, V**); 2-$CH_2CdOCOCF_3$ (**XIII, XV, XVI**), 4-$CH_2CdOCOCF_3$ (**XIV, XVII**).



We suggest the reactions in study to involve electrophilic addition of cadmium(II) trifluoroacetate to the most nucleophilic exocyclic double bond of methylene bases **VII**–**XII**. Evidently, the electrophilic activity of cadmium(II) trifluoroacetate in these reactions is higher than that of cadmium(II) acetate. As with related mercury salts [3], this is probably explained by the enhanced tendency of cadmium(II) trifluoroacetate to acquire an ionic structure like **A** due to the strong *–I* effect of the trifluoromethyl groups [4].



$$\mathrm{Cd}\begin{matrix}\diagup\mathrm{O{-}\overset{\displaystyle O}{\overset{\|}{C}}{\to}CF_3}\\ \diagdown\mathrm{O{-}\underset{\displaystyle O}{\underset{\|}{C}}{\to}CF_3}\end{matrix} \rightleftarrows [\mathrm{F_3C{\leftarrow}\underset{\displaystyle O}{\underset{\|}{C}}{-}OCd}]^{+}\,{}^{-}\mathrm{O\underset{\displaystyle O}{\underset{\|}{C}}{\to}CF_3}$$

**A**

The composition and structure of compounds **XII**–**XVIII** were confirmed by the elemental analyses (Table 1), $^1H$ and $^{19}F$ NMR and IR spectra (Table 2), mass spectra, and chemical transformations. Thus, the IR spectra contain two bands in the region of 1700–1640 cm$^{-1}$ due to carbonyl stretching vibrations of the $F_3CCOO^-$ anion and of the metal-containing fragment $CdOCOCF_3$. In addition, the IR spectra contain bands at 1178–1203 cm$^{-1}$ due to trifluoroacetate C–O vibrations and bands characteristic of various vibrations of the corresponding aromatic systems [5, 6].

In the $^1H$ NMR spectra of cadmium-containing salts **XIII**–**XVIII**, like in the specta of related mercury derivatives [2], the methylene proton signals are shifted downfield by 0.5–0.9 ppm from the $CH_3$ proton signals of the starting compounds **I**–**VI**. As

**Table 2.** IR, $^1$H, and $^{19}$F NMR spectra of compounds **XIII–XVIII, XXVI**, and **XXVII**

| Comp. no. | IR spectrum, cm$^{-1}$ | | | $^1$H NMR spectrum, δ, ppm | $^{19}$F NMR spectrum, $\delta_F$, ppm |
|---|---|---|---|---|---|
| | aromatic system | ν(C–O) | ν(C=O) | | |
| **XIII** | 1540, 1460, 865, 804, 780, 734 | 1200 | 1700, 1642 | 9.38–8.28 m (6H, quinolinium ring), 4.94 s (3H, $^+NCH_3$), 3.51 s (2H, $CH_2Cd$, $^2J_{CdH}$ 78.8 Hz) | –76.13, –76.87 |
| **XIV** | 1538, 1482, 858, 805, 775 | 1197 | 1698, 1640 | 9.32–8.18 m (6H, quinolinium ring), 4.83 s (3H, $^+NCH_3$), 3.48 s (2H, $CH_2Cd$, $^2J_{CdH}$ 72.0 Hz) | –76.11, –76.85 |
| **XV** | 1539, 1471, 866, 803, 782, 762, 726 | 1205 | 1701, 1652 | 9.29–8.25 m (6H, quinolinium ring), 4.96 q (2H, $^+NCH_2$), 3.49 s (2H, $CH_2Cd$, $^2J_{CdH}$ 81.2 Hz), 1.48 t (3H, $CH_3$) | –76.12, –76.86 |
| **XVI** | 3112, 1620, 1552, 1492, 1465, 1412, 861, 803, 778 | 1215 | 1700, 1653 | 9.58–7.92 m (11H, $C_6H_5$, quinolinium ring), 3.65 s (2H, $CH_2Cd$, $^2J_{CdH}$ 142.3 Hz) | –76.21, –77.02 |
| **XVII** | 3118, 1610, 1540, 1493, 1460, 1410, 850, 802, 780 | 1218 | 1700, 1650 | 9.59–7.94 m (11H, $C_6H_5$, quinolinium ring), 3.70 s (2H, $CH_2Cd$, $^2J_{CdH}$ 158.8 Hz) | –76.23, –77.04 |
| **XVIII** | 1628, 1590, 1522, 1480, 862, 785, 720 | 1202 | 1688, 1645 | 8.82–8.56 m (2H, pyrilium ring), 7.92–7.05 m (8H, $2C_6H_4$), 3.98 t (4H, $2OCH_2$), 3.62 s (2H, $CH_2Cd$, $^2J_{CdH}$ 152.3 Hz), 1.78–1.52 m (8H, $2CH_2CH_2$), 0.87 t (6H, $2CH_3$) | –76.31, –77.20 |
| **XXVI** | 3110, 1618, 1558, 1498, 1471, 1415, 857, 804, 775 | 625$^a$,<br>490$^a$ | | 9.52–7.88 m (11H, $C_6H_5$, quinolinium ring), 3.82 s (2H, $CH_2Sn$, $^2J_{SnH}$ 65.8 Hz) | |
| **XXVII** | 3112, 1620, 1560, 1489, 870, 834, 776, 718 | 1203 | 1700, 1648 | 9.56–7.90 m (11H, $C_6H_5$, quinolinium ring), 3.62 s (2H, $CH_2Ni$) | –76.18, –77.05 |

$^a$ ν(C–Sn).

known [7], such a downfield shift can be caused either by electron-acceptor effect of a substituent or by magnetic anisotropy. Taking into account the relatively small difference in electronegativity between hydrogen (2.1) and cadmium (1.7) [8], we can conclude that the prevailing factor here is the magnetic anisotropy of the $CdOCOCF_3$ group. Along with the major signal of the methylene group, the $^1$H NMR spectrum contains (see figure) two symmetrically located downfield and upfield satellite signals which are probably arise from spin–spin coupling between $^1$H and the natural isotopes $^{111}$Cd and $^{113}$Cd, with $^2J_{CdCH}$ constants ranging from 72 to 159 Hz. These constants are much lower that those observed for the corresponding 2- and 4-methylene-mercurated quinolinium salts (232–245 Hz) [2]. The possible reason is that valence orbitals of Cd and C overlap to a lesser extent than those of Hg and C, which is connected with the size of pertinent orbitals. The $^1$H NMR spectra of compounds **III**–**XVIII** also contain characteristic multiplets of other protons in the same regions as in the starting salts **I**–**VI.**

The $^{19}$F NMR spectra of compounds **XIII**–**XVIII** show two closely located singlets near –76 ppm [9], belonging to the $F_3CCOO^-$ and $F_3CCOOCd$ fluorines (3F).

In the mass spectra of the cationic part of salts **XIII** and **XVI**, a weak molecular ion peak was observed only in the case of compound **XVI**. The lack of $[M]^+$ in the mass spectrum of salt **XIII** is probably explained by the extremely facile cleavage of the C–Cd bond, resulting in formation of the base $[M\text{–}CdOCOCF_3]^+$ ions (100)[1] in both cases. Further decomposition of these ions occurred by pathways typical of quinoline derivatives [10].

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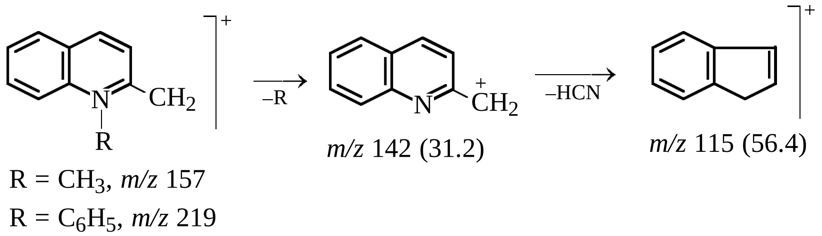
[1] Hereafter, values in parentheses are relative ion peak intensities, %.

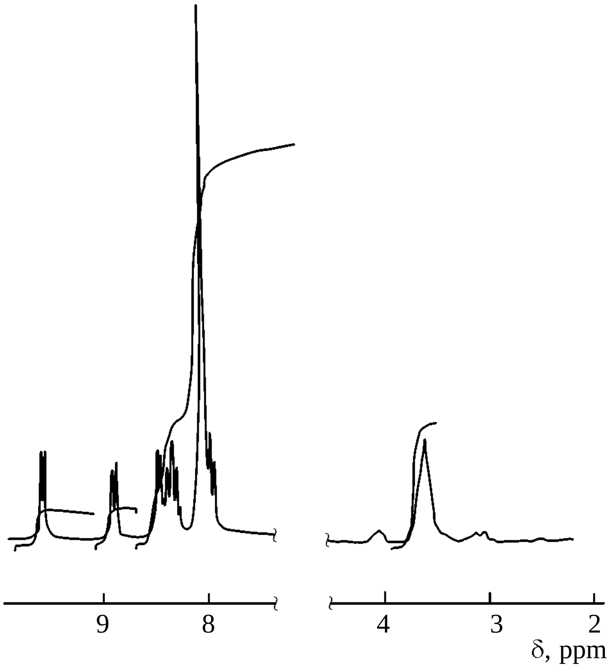


The other most abundant ion peaks in the mass spectra of compounds **XIII** and **XVI** were as follows: $[CdO]^+$ (21.5), $[Cd]^+$ (15.6), $[CF_3]^+$ (44.8), $[CF_2H]^+$ (12.7), and $[CF_2]^+$ (10.3) (*m/z* 128, 112, 69, 51, and 50, respectively).

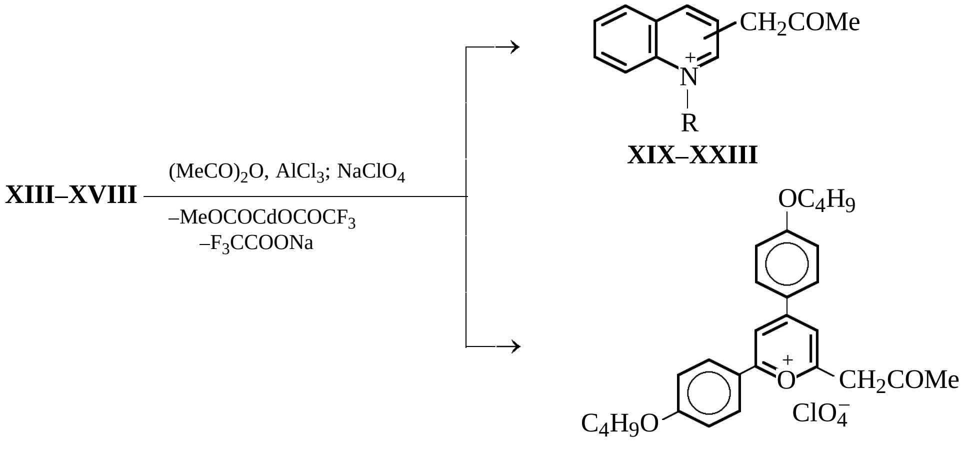
As expected, organocadmium compounds **XIII**–**XVIII** proved more reactive than related organomercury salts [1, 2]. Thus, they readily hydrolyze not only under the action of hydrochloric acid, but also in aqueous sodium perchlorate (as distinct from organomercury compounds), to give the starting compounds **I**–**VI** which were identified by the melting points and IR spectra.

The reactions of compounds **XIII**–**XVIII** with acetic anhydride in the presence of catalytic amounts of anhydrous aluminum chloride involve substitution of the $CdOCOCF_3$ group by acetyl to form known salts [11, 12] as perchlorates **XIX**–**XXIV**.

With compound **XVII** as an example we found that the $CdOCOCF_3$ group is also substituted in reactions with some anhydrous metal salts. These reactions



$^1$H NMR spectrum of compound **XVII**.



**XIII–XVIII**

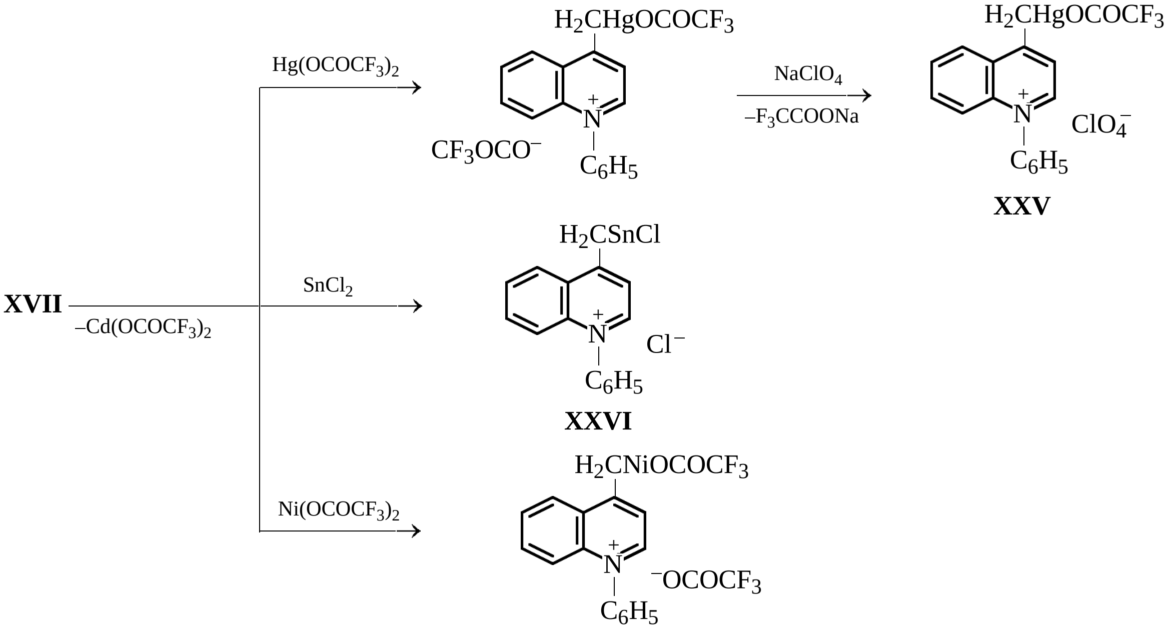
**XIX–XXIII**

**XXIV**

R = $CH_3$ (**XIX, XX**), $C_2H_5$ (**XXI**), $C_6H_5$ (**XXII, XXIII**); 2-$CH_2COMe$ (**XIX, XXI, XXII**), 4-$CH_2COMe$ (**XX, XXIII**).

readily proceed with equimolar reagent amounts in absolute ethanol under reflux. In this way, by transmetalation of salt **XVII** with mercury(II) trifluoroacetate, tin(II) chloride, and nickel(II) trifluoroacetate we obtained the previously described [2] mercury salt **XXV** identified by the melting point and IR spectrum using reference sample, and new metal-containing quinolinium salts **XXVI** and **XXVII**. The composition and structure of the latter were confirmed by the elemental analyses (Table 1) and the $^1$H NMR and IR spectra (Table 2).

Investigations on the synthetic potential of the above reactions and on the structure and properties of their products are now in progress.



**XXV**

**XXVI**

**XXVII**

Thus, cadmium-containing heterocyclic salts **XIII**–**XVIII** are highly reactive synthons for organic synthesis, and their further study is of obvious interest.

## EXPERIMENTAL

The IR spectra were registered on UR-20 or IKS-29 spectrometers in KBr pellets or in suspensions in Vaseline oil. The $^1$H and $^{19}$F NMR spectra were recorded on a Bruker WP-200SY (200.13 and 188.31 MHz) instrument in $CDCl_3$ or $(CD_3)_2CO$ (compounds **XXVI** and **XXVII**), internal references TMS and $F_3CCl$, respectively. The mass spectra of compounds **XIII** and **XVI** were run on an MKh-1320 mass spectrometer with a DS-50 system for data acquisition and treatment; ionizing energy 70 eV, ion source temperature 250°C, direct probe temperature 150–160°C.

**Cadmium(II) triflouroacetate.** To a solution of 5.3 ml of trifluoroacetic acid in 10 ml of water, 5.16 g of cadmium carbonate was added stepwise. The reaction mixture was held for 2 h at room temperature, evaporated on a water bath until precipitate formation, and cooled. The colorless crystalline precipitate was filtered off and dried in air at room temperature to constant weight to obtain 12.4 g of $Cd(OCOCF_3)\cdot 4H_2O$. The crystal hydrate was dried for 3.5 h at 120°C and then at 140° for 4 h to obtain 10.12 g of anhydrous cadmium(II) trifluoroacetate which was handled in a desiccator over $P_2O_5$.

**1-Methyl-2-(trifluoroacetoxycadmiomethyl)-quinolinium trifluoroacetate (XIII).** To a solution of 1 mmol of salt **I** in 3 ml of anhydrous acetonitrile, 1.2 mmol of sodium ethylate dissolved in 2 ml of anhydrous ethanol was added; therewith, the colorless mixture turned dark red, and a sodium perchlorate precipitate formed. After 10-min stirring, 3 ml of anhydrous diethyl ether was added, and the $NaClO_4$ precipitate was filtered off and washed with 1.5 ml of a 1 : 1 acetonitrile–ether mixture. The dark red colored filtrate was treated with 1 mmol of anhydrous cadmium(II) triflouroacetate. The reaction mixture was stirred for 15 min at 20°C, the solvent was removed in vacuo at room temperature, and the residue was washed in succession with ether and hexane and dried in a vacuum desiccator over $P_2O_5$ to obtain 0.48 g of salt **XIII**. Compounds **XIV**–**XVIII** were synthesized in a similar way (Table 1).

**2-(Acetylmethyl)-1-phenylquinolinium perchlorate (XXII).** To a solution of 0.28 g of salt **XVI** in 3 ml of anhydrous $CH_2Cl_2$, 1 ml of acetic anhydride and 0.1 g of anhydrous $AlCl_3$ were added. The reaction mixture was refluxed for 20 min with protection from air moisture, treated with 5 ml of cold water, stirred for 2 h, and filtered. The filtrate was treated with 2 ml of saturated aqueous sodium perchlorate. The light rose precipitate that formed was filtered off, washed in succession with water and ether, and dried at room temperature to constant weight to obtain 0.16 g (93%) of compound **XXII**, mp 161–163°C [11]. Salts **XIX**–**XXI**, **XXIII** and **XXIV** were synthesized in a similar way.

**4-(Trifluoroacetoxymercuriomethyl)-1-phenylquinolinium perchlorate (XXV).** A mixture of 0.5 mmol of salt **XVII** and 0.5 mmol of mercury(II) trifluoroacetate in 2 ml of anhydrous ethanol was refluxed for 30 min, 3 ml of saturated aqueous $NaClO_4$ was added, and the resulting mixture was held overnight in a refrigerator at 5–6°C. The precipitate that formed was filtered off, washed with 5 ml of cold water, and dried to constant weight to obtain 0.28 (95%) of compound **XXV**, mp 190–192°C [2].

**4-(Chlorostanniomethyl)-1-phenylquinolinium chloride (XXVI).** A mixture of 0.5 mmol of salt **XVII** and 0.5 mmol of $SnCl_2$ in 2 ml of anhydrous ethanol was refluxed for 30 min. The ethanol was removed at room temperature, and the residue was washed with 5 ml of cold water and dried to constant weight to obtain 0.071 g of salt **XXVI**. Compound **XXVII** was synthesized in a similar way (Table 1).

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