

SHORT
COMMUNICATIONS

Reaction of 2- and 4-(Acetoxymethylmercuriomethyl)-1-phenylquinolinium Perchlorates with Sodium Ethoxide

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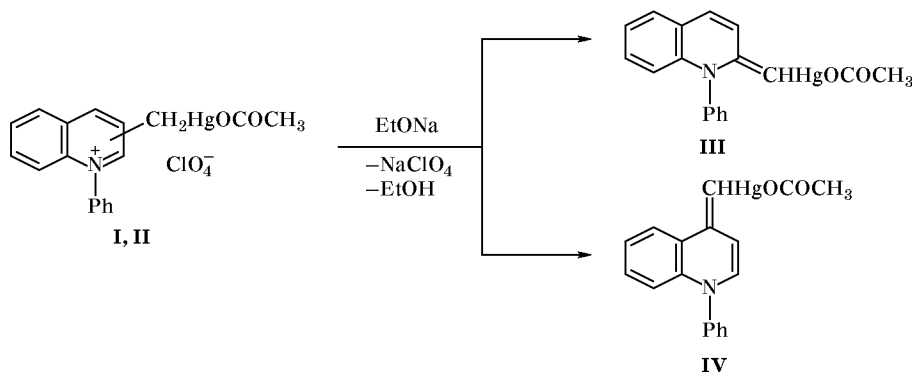
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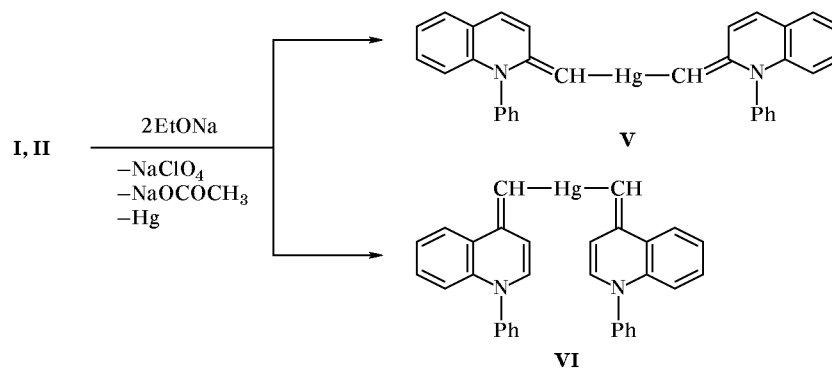
We previously developed [1] convenient methods for preparation of 2- and 4-mercuriomethylquinolinium salts **I** and **II** which turned out to be reactive toward electrophilic reagents [2]. As a result, various functionally substituted quinoline derivatives were obtained by replacement of the mercury-containing group. In addition, compounds **I** and **II** were found to exhibit biological activity [3], which makes study of their properties specifically interesting.

In the present work we examined the reaction of salts **I** and **II** with a nucleophilic reagent, sodium ethoxide. Addition of an equimolar amount of sodium ethoxide in anhydrous ethanol to a solution of salt **I** or **II** in anhydrous acetonitrile at room temperature resulted in its ready deprotonation with formation of colored mercury-containing product **III** or **IV**, respectively (Scheme 1). The reaction of salts **I** and **II** with 2 equiv of sodium ethoxide, other conditions being

Scheme 1.



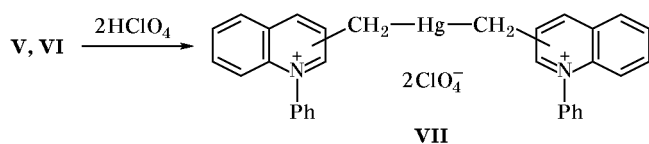
Scheme 2.



equal, afforded symmetrical mercury-containing compounds, bis(1-phenyl-1,2-dihydroquinolin-2-ylidene-methyl)mercury (V) and bis(1-phenyl-1,4-dihydroquinolin-4-ylidenemethyl)mercury (VI) (Scheme 2). The reaction was accompanied by liberation of metallic mercury.

Compounds III and IV are fairly stable in the dark at room temperature; however, they decompose with liberation of mercury on exposure to light. Acetoxymercuriomethylenequinolines III and IV are readily soluble in polar organic solvents (such as acetonitrile, DMF, ethanol, and methanol) and insoluble in water; they decompose on heating above 200°C. The structure of products III–VI was confirmed by elemental analysis, UV, IR, and ¹H NMR spectroscopy, and chemical transformations. In particular, compounds III–VI are readily protonated with perchloric acid in acetonitrile at room temperature to give initial salts I and II and previously known [4] symmetrical bisquinolinium salts VII in almost quantitative yield (Scheme 3).

Scheme 3.



On heating in hydrochloric acid, compounds III–VI undergo protodemercuration to the corresponding 2- and 4-methylquinolinium salts. Mercurated quinoline derivatives III–VI attract interest as potential nucleophilic synthons for organometallic synthesis.

2-Acetoxymercuriomethylene-1-phenyl-1,2-dihydroquinoline (III). To a solution of 1 mmol of sodium ethoxide in 1–1.5 ml of anhydrous ethanol we added a solution of salt I in 3 ml of anhydrous acetonitrile, and the mixture was stirred for 1 h at room temperature. The mixture was diluted with 20 ml of water, and the red–violet precipitate was filtered off, washed with 5 ml of water, and dried in the dark until constant weight. Yield 98%. IR spectrum, ν , cm^{-1} : 1632, 1621 (C=O, C=C); 1587, 1548, 1522, 1441 (C–C_{arom}); 1286 (C–O). ¹H NMR spectrum, δ , ppm: 1.86 s (3H, COCH₃), 4.12 s (1H, HCHg, ²J_{Hg,H} = 146 Hz), 6.36 d (1H, 4-H, ³J_{H,H} = 9.5 Hz), 6.67 d (1H, 3-H, ³J_{H,H} = 9.5 Hz), 6.97–7.82 m (9H, H_{arom}). UV spectrum, λ_{max} , nm: 400, 560. Found, %: Hg 41.49; N 2.83. C₁₈H₁₅HgNO₂. Calculated, %: Hg 41.97; N 2.93.

4-Acetoxymercuriomethylene-1-phenyl-1,4-dihydroquinoline (IV) was synthesized in a similar way.

Yield 97%. IR spectrum, ν , cm^{-1} : 1641, 1626, 1612 (C=O, C=C); 1591, 1553, 1514, 1447 (C–C_{arom}); 1286 (C–O). ¹H NMR spectrum, δ , ppm: 1.86 s (3H, COCH₃), 4.18 s (1H, HCHg, ²J_{Hg,H} = 151 Hz), 6.42 d (1H, 3-H, ³J_{H,H} = 8.9 Hz), 6.75 d (1H, 2-H, ³J_{H,H} = 8.9 Hz), 7.00–7.89 m (9H, H_{arom}). UV spectrum, λ_{max} , nm: 290, 380, 565. Found, %: Hg 39.38; N 2.49. C₁₈H₁₅HgNO₂. Calculated, %: Hg 41.97; N 2.93.

Bis(1-phenyl-1,2-dihydroquinolin-2-ylidene-methyl)mercury (V). To a solution of 2 mmol of sodium ethoxide in 1.5–2 ml of anhydrous ethanol we added a solution of salt I in 3 ml of anhydrous acetonitrile. The mixture was stirred for 2 h at room temperature and filtered, the filtrate was diluted with 20 ml of water, and the red–brown precipitate was filtered off, washed with 5 ml of water, and dried in the dark until constant weight. Yield 92%. IR spectrum, ν , cm^{-1} : 1622, 1610 (C=C); 1593, 1563, 1518, 1445 (C–C_{arom}). ¹H NMR spectrum, δ , ppm: 4.01 s (2H, HCHg, ²J_{Hg,H} = 121 Hz), 6.28 d (2H, 4-H, ³J_{H,H} = 9.2 Hz), 6.61 d (2H, 3-H, ³J_{H,H} = 9.2 Hz), 6.95–7.78 m (18H, H_{arom}). Found, %: Hg 31.42; N 4.16. C₃₂H₂₄HgN₂. Calculated, %: Hg 31.48; N 4.40.

Bis(1-phenyl-1,4-dihydroquinolin-4-ylidene-methyl)mercury (VI) was synthesized in a similar way. Yield 94%. IR spectrum, ν , cm^{-1} : 1628, 1614 (C=C); 1600, 1588, 1548, 1512, 1446 (C–C_{arom}). ¹H NMR spectrum, δ , ppm: 4.04 s (2H, HCHg, ²J_{Hg,H} = 124 Hz), 6.36 d (2H, 3-H, ³J_{H,H} = 9.00 Hz), 6.69 d (2H, 2-H, ³J_{H,H} = 9.00 Hz), 7.01–7.86 m (18H, H_{arom}). Found, %: Hg 31.45; N 4.28. C₃₂H₂₄HgN₂. Calculated, %: Hg 31.48; N 4.40.

Reaction of compounds III–VI with perchloric acid. To a solution of 1 mmol of compound III–VI in 3–4 ml of acetonitrile we added dropwise 0.3 ml of 70% aqueous HClO₄. The mixture sharply changed its color, and a yellow solid precipitated. After 0.5 h, the mixture was diluted with 15 ml of water, and the precipitate was filtered off, washed with 5 ml of water, and dried at room temperature until constant weight. The yields of products I, II, and VII were 96–98%. Their physical constants and spectral data were consistent with those reported in [1, 4].

The IR spectra were recorded on an IKS-29 spectrometer from samples dispersed in mineral oil. The ¹H NMR spectra were obtained on a Bruker WP-200SY instrument at 200.13 MHz using DMSO-*d*₆ as solvent and TMS as internal reference. The UV spectra were measured in acetonitrile on an SF-46 spectrophotometer.

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