

SHORT
COMMUNICATIONS

Synthesis of Unsymmetrical Completely Substituted Tetrazole-containing 2- and 4-Methylenemercurated Quinolinium Salts

N. A. Kopaeva, A. I. Moskalenko, E. M. Krasnikova, and V. I. Boev

Lipetsk State Pedagogical University, Lipetsk, 398020 Russia

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Organomercury derivatives of quinolinium [1] and tetrazole [2] salts are of interest for synthesis of various functional derivatives thereof finding application in medicine, biology, agriculture, and technology [3]. In extension of previously developed method for the synthesis of completely substituted symmetrical and unsymmetrical 2- and 4-methylenemercurated salts of heterocyclic cations [4] we report here on the reactions of 2- and 4-methylenemercurated quinolinium salts **I-III** [5] with tetrazolate-anions. The latter are known to readily arise on treating with alkaline reagents tetrazole (**IV**) and 5-substituted tetrazoles **V**, **VI** that are heterocyclic N-H acids [8].

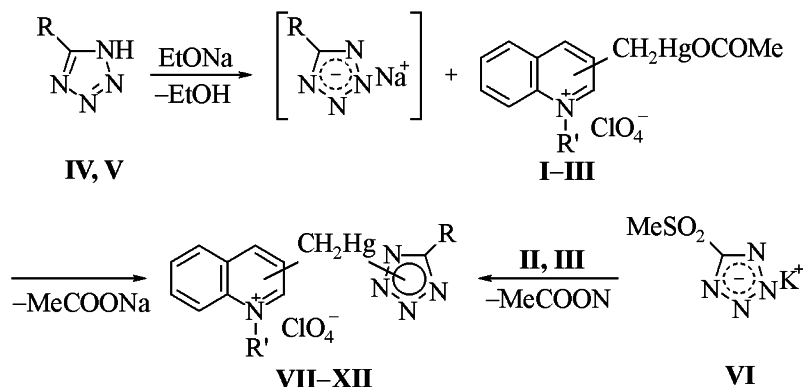
Actually, addition of sodium ethylate in anhydrous ethanol to solutions of compounds **IV**, **V** in acetonitrile gave rise in situ to the corresponding sodium salts that afterwards cleanly reacted at room temperature with an equimolar amount of salt **I-III** resulting in substitution of acetate group attached to mercury by tetrazole rest. Thus we obtained tetrazole-containing quinolinium salts **VII-X** in 76-96% yield. In the

case of 5-methylsulfonyltetrazole (**VI**), a fairly strong N-H acid [7], with salts **II**, **III** was reacted its more accessible [7] potassium salt in water-acetonitrile medium. The yields of reaction products **XI**, **XII** here also were high.

It should be noted that N-substituted tetrazoles, e.g., 1-phenyltetrazole, under the described conditions did not react with salts **I-III**.

The mercury-containing salts **VII-XII** synthesized are stable in air colored solids, insoluble in water and nonpolar organic solvents; on heating they melt with decomposition. The composition and structure of compounds **VII-XII** were confirmed by elemental analyses, IR and ¹H NMR spectra.

In IR spectra of all compounds obtained the absorption bands of acetate group characteristic of initial salts **I-III** [5] were lacking, but appeared bands of various intensity corresponding to vibrations of ClO₄⁻ group and tetrazole ring [8]. In the ¹H NMR spectra only one set of multiplet signals was observed belong-



ing to the protons from the structural fragments of compounds **VII–XII**. These data indicate that the mercuration of tetrazolate anions with salts **I–III** furnished a single N-isomer probably due to formation of delocalized σ -bonds “metal-ring” with a possible donor-acceptor interaction of the lowest occupied orbitals of tetrazolate anion and unoccupied orbitals of cation $^+ \text{HgCH}_2\text{Ht}$ with an appropriate symmetry. However assignment of compounds **VII–XII** to N¹- or N²-isomers of tetrazole requires supplementary studies.

On heating compounds **VII–XII** in hydrochloric acid they suffer protodemercuration affording salts of 2- and 4-methyl-1-R'-quinolinium and initial tetrazoles **IV–VI** identified with authentic samples by melting points and IR spectra.

1-Methyl-2- η^5 -tetrazolemercuromethylquinolinium perchlorate (VII). To a solution of 0.070 g (1 mmol) of tetrazole **IV** in 2.3 g of anhydrous acetonitrile was added 1 mmol of sodium ethylate in 0.6 ml of anhydrous ethanol, and the mixture was stirred for 0.5 h at room temperature. Then to the mixture was added 3 ml of acetonitrile, 0.516 g (1 mmol) of salt **I**, the stirring was continued for 1 h, and the reaction mixture was left standing for 20 h at room temperature. Then 20 ml of ethyl ether was added, the separated precipitate was filtered off, washed with 5 ml of water, and dried. Yield 0.468 g (89%), mp 180–182°C (decomp.). IR spectrum, η , cm^{-1} : 1098, 621 (ClO_4^-), 1015, 1049, 1081, 1260, 1436, 1458, 1508 (tetrazole). ^1H NMR spectrum, δ , ppm: 3.82 s (2H, CH_2Hg , $^2J_{\text{HgH}}$ 146 Hz), 4.31 s (3H, NCH_3), 7.36–8.78 m (6H_{arom}), 9.18 s (1H, C^5H). Found, %: Hg 38.20; N 12.96. $\text{C}_{12}\text{H}_{12}\text{ClHgN}_5\text{O}_4$. Calculated, %: Hg 38.12; N 13.30.

Compounds **VIII–X** were prepared in a similar way.

1-Phenyl-2- η^5 -2-tetrazolemercuromethylquinolinium perchlorate (VIII). Yield 85%, green-yellow crystals, mp 190–192°C (decomp.). IR spectrum, η , cm^{-1} : 1100, 620 (ClO_4^-), 1018, 1053, 1083, 1262, 1442, 1460, 1512 (tetrazole). ^1H NMR spectrum, δ , ppm: 3.96 s (2H, CH_2Hg , $^2J_{\text{HgH}}$ 151 Hz), 7.41–8.79 m (11H_{arom}), 9.23 s (1H, C^5H). Found, %: Hg 34.48; N 11.45. $\text{C}_{17}\text{H}_{14}\text{ClHgN}_5\text{O}_4$. Calculated, %: Hg 34.10; N 11.90.

1-Phenyl-2- η^5 -(5-methylthiotetrazole)mercuromethylquinolinium perchlorate (IX). Yield 89%, red-brown crystals, mp 182–185°C (decomp.). IR spectrum, η , cm^{-1} : 1100, 621 (ClO_4^-), 1028, 1048, 1080, 1273, 1481, 1526 (tetrazole), 730 (C–S).

^1H NMR spectrum, δ , ppm: 2.65 s (3H, H_3CS), 3.91 s (2H, CH_2Hg , $^2J_{\text{HgH}}$ 150 Hz), 7.39–8.68 m (11H_{arom}). Found, %: Hg 31.46; N 11.08. $\text{C}_{18}\text{H}_{16}\text{ClHgN}_5\text{O}_4\text{S}$. Calculated, %: Hg 31.63; N 11.04.

1-Phenyl-4- η^5 -(5-methylthiotetrazole)mercuromethylquinolinium perchlorate (X). Yield 87%, green crystals, mp 185–188°C (decomp.). IR spectrum, η , cm^{-1} : 1098, 620 (ClO_4^-), 1023, 1051, 1082, 1275, 1478, 1528 (tetrazole), 730 (C–S). ^1H NMR spectrum, δ , ppm: 2.65 s (3H, H_3CS), 4.01 s (2H, CH_2Hg , $^2J_{\text{HgH}}$ 152 Hz), 7.42–8.73 m (11H_{arom}). Found, %: Hg 31.12; N 11.47. $\text{C}_{18}\text{H}_{16}\text{ClHgN}_5\text{O}_4\text{S}$. Calculated, %: Hg 31.63; N 11.04.

1-Phenyl-2- η^5 -(5-methylsulfonyltetrazole)mercuromethylquinolinium perchlorate (XI). To 0.093 g (0.5 mmol) of 5-methylsulfonyltetrazole potassium salt in 1.2 ml of water was added 0.284 g (0.5 mmol) of compound **II** in 2.5 ml of acetonitrile, the mixture was stirred for 10 min at room temperature, 5 ml of water was added, the separated red-brown precipitate was filtered off, washed with water, and dried. Yield 0.32 g (96%), mp 210–212°C (decomp.). IR spectrum, η , cm^{-1} : 1100, 622 (ClO_4^-), 1054, 1076, 1084, 1408, 1470, 1506 (tetrazole), 1174, 1342 (SO_2). ^1H NMR spectrum, δ , ppm: 3.28 s (3H, Me), 3.95 s (2H, CH_2Hg , $^2J_{\text{HgH}}$ 154 Hz), 7.42–8.71 m (11H_{arom}). Found, %: Hg 29.83; N 10.62. $\text{C}_{18}\text{H}_{16}\text{ClHgN}_5\text{O}_6\text{S}$. Calculated, %: Hg 30.11; N 10.51.

Compound **XII** was prepared similarly.

1-Phenyl-4- η^5 -(5-methylsulfonyltetrazole)mercuromethylquinolinium perchlorate (XII). Yield 76%, yellow-brown crystals, mp 172–175°C (decomp.). IR spectrum, η , cm^{-1} : 1100, 621 (ClO_4^-), 1051, 1078, 1091, 1410, 1473, 1511 (tetrazole), 1175, 1344 (SO_2). ^1H NMR spectrum, δ , ppm: 3.28 s (3H, Me), 4.08 s (2H, CH_2Hg , $^2J_{\text{HgH}}$ 156 Hz), 7.43–8.75 m (11H_{arom}). Found, %: Hg 30.24; N 10.77. $\text{C}_{18}\text{H}_{16}\text{ClHgN}_5\text{O}_6\text{S}$. Calculated, %: Hg 30.11; N 10.51.

IR spectra were recorded on IKS-29 instrument from mulls in mineral oil. ^1H NMR spectra were registered on spectrometer Bruker AC-300 (300.13 MHz) in DMSO, internal reference HMDS.

REFERENCES

1. Boev, V.I., Moskalenko, A.I., Denisov, S.P., Nevstruev, A.N., Kopaeva, N.A., and Matorkina, I.A.,

- Abstracts of Papers, *VII Russian Conf. on Metalloorg. Khim.*, Moscow, 1999, vol. 2, p. 168.
- Gaponik, P.N., *Doctoral Sci. (Chem.) Dissertation*, St. Petersburg, 2000.
 - Koldobskii, G.I. and Ostrovskii, V.A., *Usp. Khim.*, 1994, vol. 63, no. 10, pp. 847–865; Pilyugin, G.T. and Gutsulyak, B.M., *Usp. Khim.*, 1963, vol. 32, no. 4, pp. 599–632.
 - Boev, V.I. and Moskalenko, A.I., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 6, pp. 1028–1031.
 - Boev, V.I. and Moskalenko, A.I., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 7, pp. 1128–1133.
 - Koldobskii, G.I., Ostrovskii, V.A., and Gidas-pov, B.V., *Khim. Geterotsikl. Soed.*, 1980, no. 7, p. 867.
 - Alam, L.V. and Koldobskii, G.I., *Zh. Org. Khim.*, 1997, vol. 33, no. 8, pp. 1224–1230.
 - Koldobskii, G.I., Ostrovskii, V.A., and Poplavskii, V.S., *Khim. Geterotsikl. Soed.*, 1981, no. 10, pp. 1299–1326.