

Elena Ghezzi, Alberto Sturaro and Pietro Traldi*

CNR, Area di Ricerca di Padova, Corso Stato Uniti 4,
I35100 Padova, Italy

Pierfrancesco Bravo and Fiorenza Viani

Dipartimento di Chimica del Politecnico, Piazza Leonardo da Vinci 32,
I20133 Milano, Italy

Received June 6, 1989

The electron impact mass spectrometric behaviour of three 2-methyl-2-chloromercuriomethyl-2,6-dihydro-5H-pyrano[3,2-c]quinolin-5-ones have been studied in detail with the aid of metastable ion data. The primary loss of C_4H_7 , necessarily involving an unusual HgCl rearrangement, is discussed and justified by the formation of a thermodynamically stable Hg-containing cyclic structure.

J. Heterocyclic Chem., **27**, 1293 (1990).

Introduction.

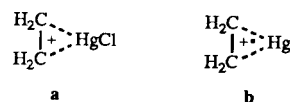
The mercuriation of unsaturated alcohols, phenols and enols provides a very useful method for the synthesis of cyclic and polycyclic five and six-membered ring ethers [1].

We have recently noted that cyclization of certain 3-alkenyl substituted 4-hydroxy-2-quinolones **1** promoted by mercuric salts involve the β -oxygen of the cyclic β -ketoamide exclusively and therefore give rise to the pyrano-[3,2-c]pyran-5-one structures **2** in a totally regioselective process [2] (see Scheme 1). In their turn halomercurio compounds **2** have been utilized in the synthesis of some naturally occurring quinolone alkaloids **3**, which, together with some similarly structured tetrahydropyranocoumarins and chromones, were the object of previous mass spectrometric investigations [3,4].

Mass spectrometric studies on compounds **2** have never been reported until now, also whether data on organomercury compounds are available in literature [5-7].

Briant and Kinstle in a systematic study on the electron impact induced fragmentation processes of diaryl- and dialkyl-mercury compounds and aryl- and alkyl-mercurio halides, observed that the cleavage of the C-Hg bond with the retention of the charge on the organic moiety, was present in all the examined compounds [5]. The occurrence of β cleavage in the two classes of compounds was also

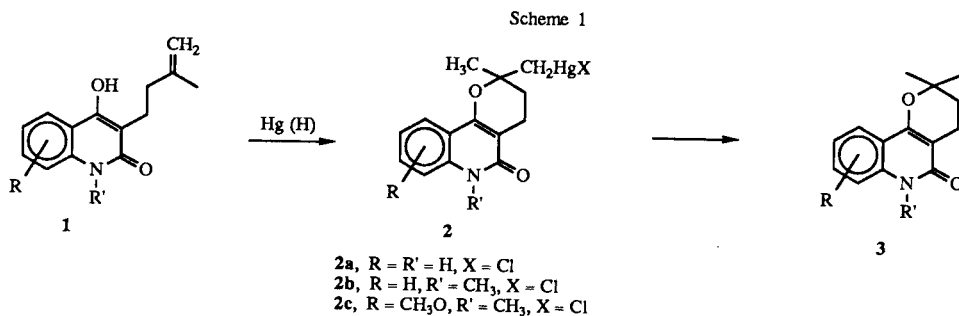
observed, and justified with the formation of highly stable ions as **a** and **b**.



Brewer *et al.*, studying a series of organomercury compounds, put in evidence the existence of some complex rearrangement processes concurrent with Hg loss, observed in the case of diaryl Hg derivatives, well justified by the high stability of the product ions. Furthermore, in the case of alpha-mercurated carbonyl compounds a clear difference between aldehydes and ketones was found, *i.e.* only in the former case Hg extrusion was observed and in the latter the alpha-cleavage to the carbonyl resulted, quite surprisingly, more favoured with respect to the Hg-C bond [6].

Finally Glockling *et al.* observed, in the case of mercurio halides also the metastable supported loss of X^{\bullet} , implicating the cleavage of Hg-X bond, never described before [7].

In the present paper we will discuss the mass spectrometric behaviour of the three chloromercurio compounds **2a-2c**, as obtained by B/E = const linked scans [8] and mass analyzed ion kinetic energy spectrometry [9].



Scheme 2

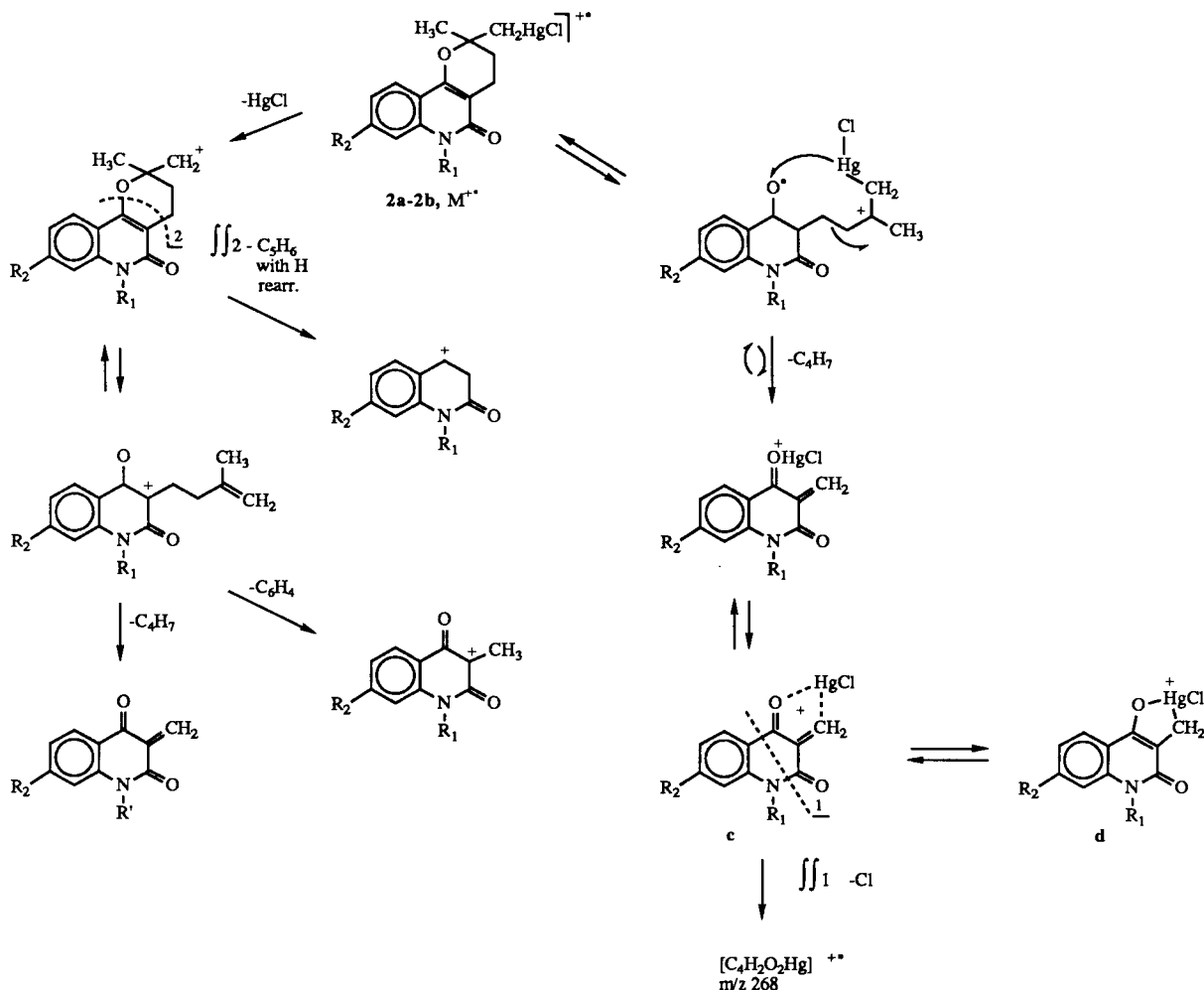


Table 1 - 70 eV EI mass spectra of compounds 2a - 2c
(The m/z values are these due to ³⁵Cl and ¹⁹⁸Hg isotopes)

COMPOUNDS	2a	2b	2c
M ⁺	465 (5)	479 (5)	509 (0.5)
[M - C ₄ H ₇] ⁺	410 (2)	424 (100)	454 (0.2)
[M - HgCl] ⁺	228 (100)	242 (100)	272 (20)
[M - HgCl - C ₄ H ₆] ⁺	174 (95)	188 (37)	218 (100)
[M - HgCl - C ₄ H ₇] ⁺	173 (14)	187 (18)	217 (5)
[M - HgCl - C ₃ H ₅ O]	172 (14)	186 (51)	216 (1)
[M - HgCl - C ₅ H ₆]	146 (4)	160 (2)	190 (7)
[M - C ₄ H ₇ - R ₂ C ₈ H ₃ NR ₁]	268 (3)	268 (7)	268 (1)

EXPERIMENTAL

Mass Spectrometric Measurements.

All mass spectrometric measurements were performed on a

double focusing, reverse geometry VG ZAB2F instrument operating in EI conditions (70 eV, 200 μA).

Metastable transitions were detected by B/E linked scans [8] and mass-analyzed ion kinetic energy (MIKE) spectra [9].

Synthesis of 2a-2c.

Compounds 2a-2c have been obtained as follows:

Selective 3-monoalkylation of 4-Hydroxy-2(1H)-quinolinones with 4-Dimethylamino-2-butanone and methylenation of the side-chain carbonyl group of the adducts so formed by treatment with methylenetriphenylphosphorane, gave the corresponding 4-Hydroxy-3-(3-methylbut-3-enyl)-2(1H)-quinolinones. The selective cyclization of those olefins to the 2-chloromercuriomethyl-3,4-dihydro-2H,5H-pyrano[3,2-c]quinolin-5-ones 2a-2c have been realized by mercury(II) acetate treatment followed by the exchange of the acetate by chlorine anion.

Results and Discussion.

The 70 eV EI mass spectra of compounds 1-3 are reported in Table 1.

The only metastable supported primary decomposition pathway arise from the cleavage of the C-Hg bond and from the loss of C₄H₇. While the former has been always described in EI mass

spectrometry of organomercurio halides, the latter, necessarily requiring an HgCl rearrangement, has never been observed. The kinetic energy release related to this decomposition pathway was found to be the range 180-250 meV for all the examined compounds, suggesting the formation of thermodynamically stable ionic species.

Looking at the already published data on some related 2,2-dimethyl-substituted alkaloids, it is reasonable to assume that these primary decompositions originate through the concurrent C-Hg and O-C (**2**) cleavages (see Scheme 2).

These fragmentation processes generate two different sets of fragment ions, such as those in the right and left parts of Scheme 2. The maintenance of Hg-C bond in some fragmentation products is noteworthy. As already suggested by Brian and Kinsley, it can be justified by the formation of cyclic structures, highly stable from the thermodynamic point of view.

Hence, for the $[M-C_4H_7]^+$ ion formation we propose a C-O bond cleavage followed by intramolecular HgCl shift on the oxygen, followed by a C-C bond cleavage and loss of the aliphatic side chain. For the ions so formed, structures **c** and **d** of Scheme 2 can be reasonably proposed.

The successive cleavage of the *N*-containing ring, leading to $[C_4H_2O_2Hg]^+$ ions, is in agreement with those structures. Cyclic structures with the mercury bound to a carbon atom and to a contiguous oxygen are quite common (1); they are formed for example by thermal decomposition of the mercury(II) salts of aromatic *ortho* dicarboxylic acids.

Anyway, it must be stressed that most of the total ion current is retained by organic ions all originating from the $[M - HgCl]^+$ ions, through decomposition mechanisms analogous to those described for the 2,2-dimethyl derivatives. Thus, while the loss of C_5H_6O can be easily explained by cleavage **2** of Scheme 2, the losses of hydrocarbon moieties (C_4H_6 and $C_4H_7^+$) can be justified considering ions of structures **e** (Scheme 2), analogous to those already invoked in mass spectrometric studies of quinolone alkaloids, tetrahydropropano-coumarins and chromones [3,4].

REFERENCE AND NOTES

- [1] R. C. Larock, *Sulfomercuration Demercuration Reactions in Organic Synthesis*, Springer Verlag, Berlin, 1986.
- [2] P. Bravo, G. Resnati, F. Viani and G. Cavicchio, *Gazz. Chim. Ital.*, **118**, 507 (1988).
- [3] A. Sturaro, P. Traldi, P. Bravo, F. Viani and G. Resnati, *Org. Mass Spectrom.*, **22**, 246 (1987).
- [4] P. Bravo, C. Ticozzi, S. Daolio and P. Traldi, *Org. Mass Spectrom.*, **20**, 740 (1985).
- [5] W. F. Bryant and H. Kinstle, *J. Organomet. Chem.*, **24**, 573 (1970).
- [6] S. W. Brewer, T. E. Fear, P. H. Lindsay and F. G. Thorpe, *J. Chem. Soc. C*, 3519 (1971).
- [7] F. Glocking, J. G. Irwin, R. J. Morrison and J. J. Sweeney, *Inorg. Chim. Acta*, **19**, 267 (1976).
- [8] A. P. Bruins, K. R. Jennings and S. Evans, *Int. J. Mass Spectrom. Ion Phys.*, **26**, 395 (1978).
- [9] R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam, (1973).