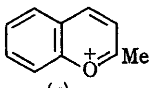
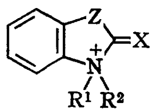
The Formation of a Five-membered-ring Ion on Electron Impact

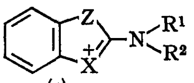
By M. A. BALDWIN, A. G. LOUDON, ALLAN MACCOLL, and D. SMITH
(*William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London, W.C.*1)
and A. RIBERA
(*Instituto de Quimica "Alonso Barba," Serrano* 119, *Madrid, Spain*)

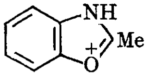
RECENTLY as part of a general programme[1] we have investigated the behaviour under electron impact of phenyl- and substituted phenyl-ureas, thioureas, and carbamates.[2] In the compounds having a substituted phenyl residue with *ortho*-chlorine atoms, a large $M-$Cl ion is observed (see Table). However, when the substituted phenyl residues have only *meta*- or *para*-chlorine atoms, then the $M-$Cl ion is less than 0·5%, as observed for some thirty compounds.

Thus a particular mechanism must be operating in the case of the *ortho*-chloro-compounds. Any electronic effect might be expected to work for both the *ortho*- and *para*-positions. Since this is not the case, this leaves as the most likely explanation the formation of a cyclic ion similar to those reported by Williams[3] and by Waight.[4] In both these cases six-membered-ring ions with a conjugated carbonyl group were postulated. The simplest case was that of methyl cinnamate where the large $M-1$ ion was thought to have the structure (*a*).


(*a*)


(*b*)


(*c*)


(*d*)

$X = Z = O$, $R^1 = R^2 = Me$;
$X = O$, $Z = NH$, $R^1 = H$, $R^2 = Ar$
or $R^1 = R^2 = Alk$;
$X = S$, $Z = NH$, $R^1 = H$, $R^2 = H$ or Ac.

In the present case, a six-membered ring is impossible and since all the monochloroanilines show an $M-$Cl ion of similar intensity, a three-membered ring can be ruled out. This leaves the possibility that the ring formation involves either the remote nitrogen (*b*) or more likely the thiocarbonyl or carbonyl grouping (*c*).

TABLE

Compounds: o-Cl·C_6H_3(R)·NH·CO·N(R′)$_2$

R	R′	(M—Cl) %	(M—Cl)/M
H	Me	36	4·5
4-Me	Me	38	3·6
5-Cl	Me	24	7·5
6-Me	Me	62	12·3
4-Me	Et	33	1·8
5-Cl	Et	25	4·9
5-Cl	*n*-Pr	19	3·4

Compounds: o-Cl-C_6H_3(R)·NH·CO·NH·C_6H_3R′R″

R	R′	R″	(M—Cl) %	(M—Cl)/M
H	H	H	8·5	0·5
6-Me	H	H	32	2
H	2-Me	H	5·3	0·3
H	2-Cl	H	7·9	0·9
H	2-MeO	H	3·8	0·1
3-Cl	2-Cl	3-Cl	3·6	1·0
5-Cl	2-Cl	5-Cl	11	2·4
6-Me	2-Cl	6-Me	50	17

Compounds: o-Cl-C_6H_4·NH·CS·NHR′

R′	(M—Cl) %	(M—Cl)/M
H	100	>100
Ac	31	>100

Compounds: o-Cl-C_6H_3(R)O·CONMe$_2$

R	(M—Cl) %	(M—Cl)/M
3-Cl	7·4	25
6-Cl	1·8	2·3
5-Cl	8·4	16

To help decide between the ions (*b*) and (*c*), the mass spectra of the acetates of the three monochloroanilines were determined. The *ortho*-compound still showed a large $M-\text{Cl}$ ion which was not shown by the *meta*- or *para*-compounds. This presumably must be (*d*) which suggests that (*c*) is a possible representation in the other cases but does not exclude (*b*) as a further possibility.

In the ureas this phenomenon seems to be effectively restricted to the loss of an *ortho*-chlorine atom. Thus in the phenyl- and substituted phenyl-ureas not containing an alkylated nitrogen, the $M-1$ ion is less than 0·5%. So the loss of an *ortho*-hydrogen by this mechanism is very small. Similar remarks apply to *ortho*-methyl- and -methoxy-substituents. This discrimination may be due to the relative weakness of the carbon–chlorine bond.

In contrast to the arylureas, the phenyl-, the two diphenyl- and the triphenyl-thioureas all show noticeable (5—10%) $M-1$ ions, presumably due to the formation of the ion (*c*). The easier formation of this ion in the case of the sulphur compounds is reflected in the more pronounced $M-\text{Cl}$ ion in the spectra of the two *o*-chlorophenylthioureas. Other substituents remain to be investigated.

Thus the formation under electron impact of a five-membered-ring ion in these compounds has been demonstrated. This, apart from one possible example,[5] is believed to be the first example of such a five-membered ring.

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[3] D. H. Williams in "Newer Physical Methods in the Study of Structural Chemistry," Laboratory Practice, London, 1967.

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