

HYDANTOINS, THIOHYDANTOINS, GLYCOCYAMIDINES. Part. XIX.<sup>x</sup>  
THE TAUTOMERISM OF 2-METHYLTHIO-4,4/5,5/-DIPHENYL-2-IMIDAZOLIN-  
-5/4/-ONE: FIRST UNEQUIVOCALLY ESTABLISHED CASE OF TAUTOMERISM  
IN THE SERIES OF HYDANTOIN DERIVATIVES.

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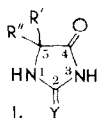
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The possibility of tautomerism amongst derivatives of hydantoin has often been discussed, see eg. /1/. Accordingly eg. 2-thiohydantoin should theoretically be able to exist in part or all of the forms Ia, IIa, IIIa, IV-VII and VIIIa:

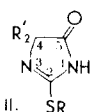
By replacing part of or all the four hydrogen atoms, responsible for the potential tautomeric changes, by alkyl groups the number of theoretically possible tautomerides becomes considerably reduced. Thus, the S-methyl derivative of 5,5-diphenyl-2-thiohydantoin /Ib/ may theoretically exist in only three tautomeric forms, viz. IIb, IIIb and VIIIb.

<sup>x/</sup> For Part XVIII. see: K. Lempert and K. Zauer: Tetrahedron Letters 1964, No 10, p. 519

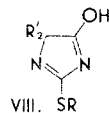
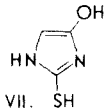
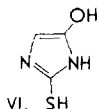
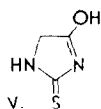
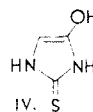
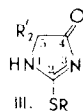
<sup>1/</sup> E. Ware: Chem. Revs. 46, 449 /1950/, and original papers cited therein



- a:  $R' = R'' = H, Y = S$   
 b:  $R' = R'' = Ph, Y = S$   
 c:  $R' = PhCH_2,$   
 $R'' = H, Y = O$



- a:  $R = R' = H$   
 b:  $R = Me, R' = Ph$



- a:  $R = R' = H$   
 b:  $R = Me, R' = Ph$

The facts hitherto considered as evidence for the existence of different tautomeric forms of hydantoins /1/ are actually by no means compelling. For instance, the formation of derivatives of different tautomeric forms by substitution starting from the same parent substance does not prove the existence of the respective particular tautomeric forms of this substance for, as has been shown by Nesmeyanov and Kabachnik /2/, derivatives of a given tautomeride may be formed, without intermediate formation of this particular form, directly from another tautomeride.

2/ A. N. Nesmeyanov: Experientia, Suppl. II., 49 /1955/;  
 A. N. Nesmeyanov and M. I. Kabachnik: Zhur. Obshchei Khim.  
25, 41 /1955/

The easy racemization by dilute alkali of optically active 5-benzyl-hydantoins /Ic/ and similar derivatives, but not of 5-ethyl-5-methyl-hydantoin, which has been accepted as evidence for the existence of enolic forms of type IV, VI or VII, on the other hand also does not really prove this assumption, for racemization could proceed, instead through enolization, rather through ionisation.

In the course of an investigation of the IR spectra of a series of hydantoin derivatives we have now found the first compelling evidence for the existence of tautomeric, moreover of desmotropic forms in the case of a derivative of hydantoin.

By using different procedures for the purification of the S-methyl derivative of 5,5-diphenyl-2-thiohydantoin, the compound hitherto named 2-methylthio-4,4/5,5/-diphenyl-2-imidazolin-5/4/-one, viz. recrystallisation a./ from ethanolic pyridine and b./ from chloroform with subsequent addition of petrolether and c./ sublimation at reduced pressure we obtained three samples of this compound, the IR spectra of the second and third being identical /see fig. 2./ but differing considerably from that of the first /see fig. 1./

Thus, although both spectra contain bands corresponding to the C=O and C=N stretching vibrations they differ in the position of this bands, see table 1.

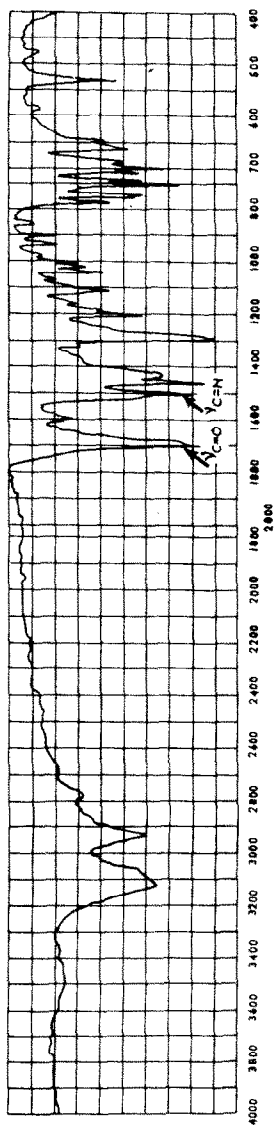


FIG. 1.

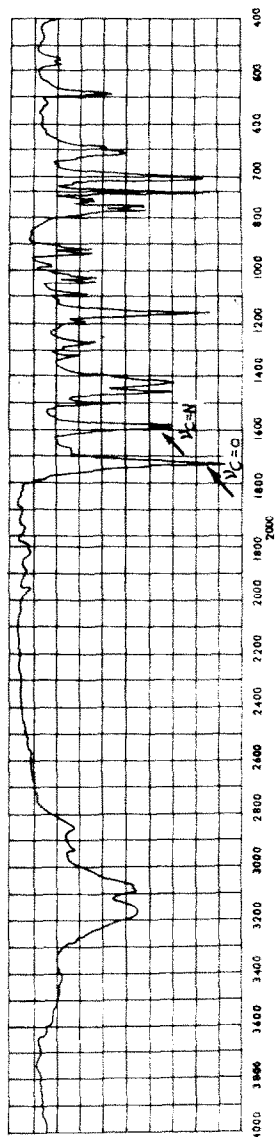


FIG. 2.

T A B L E 1.		
Sample	C=O	C=N
	Stretching frequency	
a	1690 $\text{cm}^{-1}$	1510-1490 $\text{cm}^{-1}$
b and c	1720 $\text{cm}^{-1}$	1590-1575 $\text{cm}^{-1}$

The interpretation of these differences is obvious: in sample a/ the C=O and C=N groups are conjugated to each other whereas in samples b/ and c/ they are not. Thus sample a/ corresponds to structure IIIa and samples b/ and c/ to structure IIa. The name 2-methylthio-4,4/5,5/-diphenyl-2-imidazolín-5/4/-on should, therefore, no longer be used, its "components" referring to two, actually existing, different compounds.

Evidence for the existence of the third tautomeride, viz. VIIIa is still missing.

The two tautomerides IIa and IIIa are, by the purification methods mentioned above, mutually interconvertible. Thus, we have to deal with a true tautomeric equilibrium, this being the first unequivocally established case of tautomerism in the series of hydantoin derivatives and, as far as we could ascertain, in the group of ureides, on the whole. Determination of the rates of the two opposite reactions /IIa  $\rightleftharpoons$  IIIa/ as well as of the equilibrium constant shall be shortly started.

In agreement with the differences in chemical structure, there are also considerable differences in the crystal structure as evidenced by the Debye-Scherrer diagrams<sup>x</sup> which shall be described elsewhere. It is interesting to note, however, that slight but marked differences exist also between the Debye-Scherrer diagrams of the chemically identical samples b/ and c/ and that, in contrast to these differences, the mp.-s of all three samples as determined in the Koffler block are identical.

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<sup>x/</sup> These have been recorded by Dr. G. Bidló /Dept. of Mineralogy and Geology of the Technical University, Budapest/.