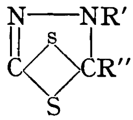
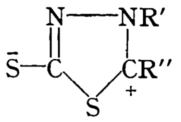
158. *The Constitution and Isomerism of Certain Triazole Derivatives of the Nitron Type in the Light of the Bredt Rule and the Theory of Resonance.**

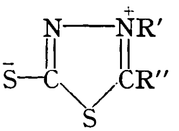
By Alexander Schönberg.

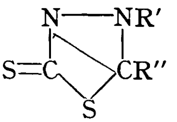
The generally accepted formula of certain di- and tri-azole derivatives is not in accordance with the laws of stereochemistry. These substances have hitherto been regarded as containing condensed ring systems, but now they are regarded as "Zwitterione." In certain cases (compare X) the old formula must be replaced by *two* different formulæ [compare VIII*a* and VIII*b* (R = Ph, R′ = CH_2Ph)] representing two isomerides. In this, as in other cases, the existence of two isomerides has been established, a phenomenon which could not be explained by the classical formula.

The chemical properties of certain *endo*thiodihydrothiodiazoles have been thoroughly investigated, especially by Busch and his co-workers (cf. *J. pr. Chem.*, 1903, **67**, 201—264, where other references are also given), and they are generally regarded as having the structure


(I.)


(II.)

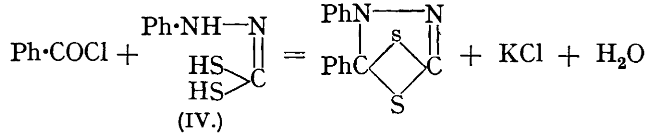

(III.)

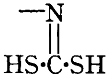

(III*a*.)

(I). This formula, however, does not conform to Bredt's rule (*Annalen*, 1924, **437**, 1) that, in the simpler polycyclic compounds, as in five- and six-membered rings, a double bond is never attached to the carbon atoms at the end of the bridge: recognition of this rule led to the revision of the formula of santene *inter alia*.

Notwithstanding this, formula (I) might be valid if it represented labile compounds, but actually those of this type are very stable to heat; *e.g.*, (I; R′ = R″ = Ph) has m. p. 224°. The reaction mechanism (A) given by Busch and his co-workers for the formation of these compounds cannot be used as support for the polycyclic formula advanced by them, since in (IV) the valencies are distorted; *i.e.*, the two univalent groups are situated on one side of a double bond, whereas in reality they are situated one on each side as in (IV*a*).

(A.)




(IV*a*.)

(i) The suggestion is now advanced that these *endo*thiodihydrothiodiazoles should be regarded as compounds with intramolecular ionogenic bonds (cf. II) and the modern views of resonance are applied in this connexion. These compounds are accordingly to be regarded as resonance hybrids between (II) and (III) and the other possible formulæ according to the theory of resonance. The new formulation takes Bredt's rule into account and is in excellent agreement with the chemical properties of this class of compound—*e.g.*, (V; R′ = R″ = Ph) is formed in a few minutes by boiling (I) with an alcoholic solution of methyl iodide (Busch, Kamphausen, and Schneider, *J. pr. Chem.*, 1903, **67**, 222); on the older idea this involves a breaking of the C–S–C bond which, under such conditions, is most improbable, but if (I) is replaced by (II) or (III) the formation of (V) is easily understandable

(ii) Considerations similar to those given above lead to rejection of the classical formulæ for the *endo*iminotriazolines, also known as *endo*iminodihydrotriazoles (cf. Wittig,

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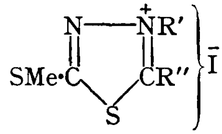
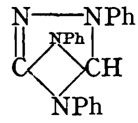
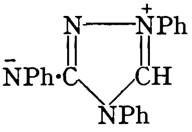
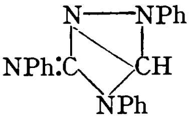
[*] See Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606; Arndt and Eistert, *Z. physikal. Chem.*, 1935, *B*, **31**, 125; Sidgwick, J., 1937, 694; General Discussion on Dipole Moments, *Trans. Faraday Soc.*, 1934, **30**, 677, which gives other references. (Added in proof) See also Ingold, *Nature*, 1938, **141**, 314; Kenner, *ibid.*, p. 786.

" Stereochemie," p. 179, in connexion with the strain properties in *N*-ring systems and the Bredt rule). It is therefore now proposed to use the betaine structure (VII) instead of (VI) for nitron, which is a pale yellow compound of high m. p. (231°). The resonance theory may also be applied to (VII).

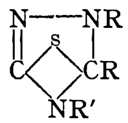

(V.)

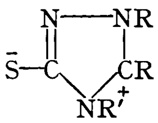

(VI.)

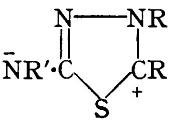

(VII.)

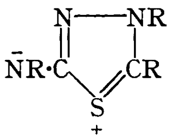

(VII*a*.)

(iii) The application of the above ideas to the *endo*thio- and *endo*oxy-triazolines (known also as *endo*thio- and *endo*oxy-dihydrotriazoles respectively) leads to the possibility of new isomerides, for *each* of the classical formulæ must be replaced by *two betaine* formulæ. For instance, (VIII) has hitherto been used for the two isomers (VIII*a*) and (VIII*b*), but now for compounds of this series it will be necessary to determine whether they are *S*-(VIII*b*) or *N*-*cyclo*-compounds (VIII*a*): each formula represents a distinct compound and to each isomer the rules of mesomerism are applicable, so that (VIII*b*) may be replaced by (VIII*c*). Similar considerations apply to the oxygen analogues (cf. IX).


(VIII.)


(VIII*a*.)

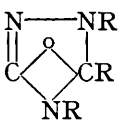

(VIII*b*.)

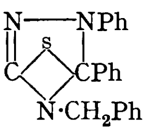

(VIII*c*.)

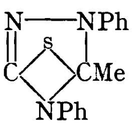
The puzzling isomeric properties of the *endo*thiotriazolines are explained by the above considerations and it is now no longer necessary, as was formerly the case in a number of instances, to represent by *one* formula *two* compounds with quite different m. p.'s. For example, the compound previously represented by (X) occurs in pale yellow needles, m. p. above 250° (mostly at 255—256°), and decomposes on standing into a crystalline powder which, recrystallised from chloroform–alcohol, has m. p. 236° (Busch, Kamphausen, and Schneider, *loc. cit.*, pp. 218, 228). Further, the disagreement between Busch and Renner (*Ber.*, 1934, **67**, 386) on the one hand and McKee (J., 1915, **107**, 1135) on the other is explained, for our conception requires that the compound previously formulated as (XI) should occur in two forms (cf. VIII*a* and VIII*b*). Since the form of m. p. 256° is readily converted into that of m. p. 233°, it seems impossible to establish by chemical means which of the isomers belongs to the *S*-series and which to the *N*-series.

(iv) It still remains to be decided whether for the dihydrotriazole derivatives mentioned in this paper formulæ containing three-membered rings should be assigned instead of the betaine formulæ; *e.g.*, whether nitron should be formulated as (VII*a*). This structure is untenable, however, for nitron is " extraordinarily stable to hydrochloric acid at higher temperatures " (Busch, *J. pr. Chem.*, 1906, **74**, 535), whereas a compound of formula (VII*a*) would certainly under such conditions yield aniline.

Similarly, (I) cannot be replaced by (III*a*) instead of by (II), for these compounds are very stable to mercuric oxide even when they are in boiling benzene solution, and such stability is quite incompatible with the presence of the $>C{=}S$ group which (III*a*) demands (Busch, *loc. cit.*, p. 204; cf. also Schönberg, van Vargha, and Paul, *Annalen*, 1930, **483**, 109).


(IX.)


(X.)


(XI.)

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[*Received, December 9th,* 1937.