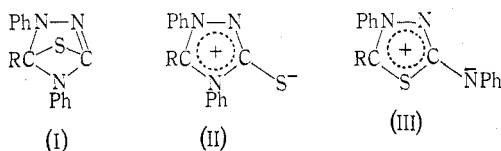


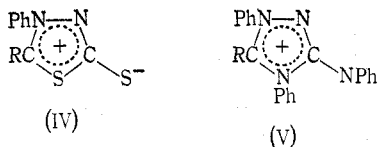
THE STRUCTURE OF THE "ENDOTHIOTRIAZOLINES" AND "ENDOXYTRIAZOLINES"

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In 1903 Busch and Schneider¹ prepared a compound A, of empirical formula $C_{14}H_{11}N_3S$, by heating 1,4-diphenylthiosemicarbazide with formic acid. They named it an "endothiotriazoline" and proposed the structure (I; $R = H$). Subsequently Baker and Ollis² proposed that this was a meso-ionic compound, for which they suggested two alternative structures (II; $R = H$) and (III; $R = H$).



The related "endothiodihydrothiadiazoles"³ and "endoiminotriazolines",⁴ also prepared by Busch *et al.*, were formulated as (IV) and (V) by Baker and Ollis.² Since the relative positions of the ring atoms in (IV) and (V) are unambiguous, comparison of the proton magnetic resonance spectra of these compounds (IV, V; $R = H$) with Busch's "endothiotriazoline" (A) should establish which of the two



structures, (II) and (III), is the more probable. The p.m.r. data, given in Table 1, indicate that the non-benzenoid proton of A has a similar environment to that of (V). Thus we favour the skeletal structure (II) for the "endothiotriazolines". Treatment of the methiodide of A with hot aqueous alkali gives 1,4-diphenylsemicarbazide and methanethiol (identified by gas chromatography), providing chemical evidence for the presence of an exocyclic sulphur atom, as in structure (II). Potts *et al.*,⁵ in a preliminary report, also claim that some of Busch's bridged-ring compounds have meso-ionic structures belonging to the 1,2,4-triazole series.

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¹ Busch, M., and Schneider, S., *J. prakt. Chem.*, 1903, **67**, 246.

² Baker, W., and Ollis, W. D., *Q. Rev. chem. Soc.*, 1957, **11**, 15.

³ Busch, M. *et al.*, *Ber. dt. chem. Ges.*, 1895, **28**, 2635; *J. prakt. Chem.*, 1899, **60**, 225; 1903, **67**, 201, 216, 246, 257.

⁴ Busch, M., *et al.*, *Ber. dt. chem. Ges.*, 1905, **38**, 856, 4049; *J. prakt. Chem.*, 1906, **74**, 533.

⁵ Potts, K. T., Roy, S. K., and Jones, D. P., *Am. chem. Soc. Abstr.*, 152nd Meeting, 1966, S-15.

The p.m.r. data for the methyl derivatives of A, (IV; R = Me), and (V; R = Me) also favour the skeletal structure (II; R = Me) for the substituted "endothiotriazolines" (see Table 1). However, Potts *et al.*⁵ claim that the product

TABLE 1
PROTON MAGNETIC RESONANCE ABSORPTIONS
(In trifluoroacetic acid)

Compound	M.P.		δ (p.p.m.)		
	Obs.	Lit.	H	CH ₃	Ph
A	216–217° ^a	214–215° ^e	9.90	—	7.5–8.0
(IV; R = H)	194–195	190 ^f	10.45	—	7.5–8.0
(V; R = H)	187–188	189 ^g	9.53	—	7.3–8.0
B	263–265 ^b	256 ^h	9.53	—	7.6–7.7
A (Me deriv.)	260–263	253°	—	2.67	7.4–7.9
(IV; R = CH ₃)	221–222°	216 ^f	—	2.97	7.4–7.8
(V; R = CH ₃)	251–252 ^d	245–246 ⁱ	—	2.58	7.2–7.9

^a Prisms from ethanol (Found: C, 66.2; H, 4.5; N, 16.5; S, 12.7. Calc. for C₁₄H₁₁N₃S: C, 66.4; H, 4.4; N, 16.6; S, 12.7%).

^b Needles from dimethylformamide (Found: C, 70.8; H, 4.9; N, 17.7. Calc. for C₁₄H₁₁N₃O: C, 70.9; H, 4.6; N, 17.7%).

^c Yellow plates from acetonitrile (Found: C, 51.3; H, 4.2; N, 13.7. Calc. for C₉H₈N₂S₂: C, 51.9; H, 3.9; N, 13.5%).

^d Pale yellow prisms from acetonitrile (Found: C, 76.6; H, 5.7; N, 17.2. Calc. for C₂₁H₁₈N₄: C, 77.3; H, 5.6; N, 17.2%).

^e Busch, M., and Schneider, S., *J. prakt. Chem.*, 1903, **67**, 246.

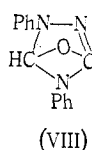
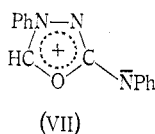
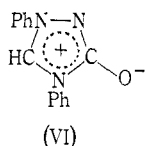
^f Busch, M., *Ber. dt. chem. Ges.*, 1895, **28**, 2635.

^g Busch, M., *Ber. dt. chem. Ges.*, 1905, **38**, 856.

^h Busch, M., and Schneider, S., *J. prakt. Chem.*, 1903, **67**, 263.

ⁱ Busch, M., and Mehrtens, G., *Ber. dt. chem. Ges.*, 1905, **38**, 4049.

of reaction of acetic anhydride and 1,4-diphenylthiosemicarbazide is 3-methyl-1,4-diphenyl-1,2,4-triazoline-5-thione (in which a phenyl group has migrated), rather than (II; R = Me). Certainly, the ultraviolet spectra of A and the corresponding methyl derivative differ appreciably, suggestive of a rearrangement of phenyl substituents.



Busch and Schneider⁶ also prepared a compound B, of empirical formula C₁₄H₁₁N₃O, by heating the 1-formyl derivative of 1,4-diphenylsemicarbazide. Their formula (VIII) was discounted by Baker and Ollis² who proposed two alternative

⁶ Busch, M., *et al.*, *J. prakt. Chem.*, 1903, **67**, 263; *Ber. dt. chem. Ges.*, 1910, **43**, 3001.

structures, (VI) and (VII). The similarity of the p.m.r. spectra of B and (V; R = H) suggests that the skeletal structure (VI) is more likely than (VII), and this is substantiated by the presence of a strong absorption at 1665 cm^{-1} , attributable to the carbonyl stretching vibrations of an amide, in the infrared spectrum of B.

Experimental

Proton magnetic resonance spectra were determined on a Varian A60 spectrometer operating at 60 Mc/s (tetramethylsilane as internal standard) using 10% solutions.

With the exception of the two compounds described below, all others were prepared according to the original literature.

The "Endothiotriazoline" A (Methyl Derivative)

A mixture of 1,4-diphenylthiosemicarbazide (1.0 g) and acetic anhydride (2.5 ml) was heated on a steam-bath for 4 hr, cooled, and diluted with water. Trituration of the resulting oil with ether gave the product (0.22 g), m.p. $260\text{--}263^\circ$ (lit.¹ 253°), after recrystallization from ethanol (Found: C, 67.6; H, 5.0; N, 15.6; S, 12.3. Calc. for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{S}$: C, 67.4; H, 4.9; N, 15.7; S, 12.0%).

The "Endothiodihydrothiodiazole" (IV; R = H)

An excess of peracetic acid (20% solution in acetic acid) was added dropwise to a solution of 4-phenyl-1,3,4-thiadiazolidine-2-thione⁷ (1.8 g) in acetic acid (25 ml) at room temperature. The corresponding disulphide⁷ (1.6 g) soon began to separate as orange crystals. These were washed with a little ethanol and then heated in chloroform at 50° for 2 hr. The product (0.7 g) separated on cooling, and gave yellow needles, m.p. $194\text{--}195^\circ$ (lit.⁷ 190°), after crystallization from chloroform/ethanol (Found: C, 49.4; H, 3.3; N, 14.5; S, 33.2. Calc. for $\text{C}_8\text{H}_6\text{N}_2\text{S}_2$: C, 49.5; H, 3.1; N, 14.4; S, 33.0%).

Ultraviolet Spectra

The "endothiotriazoline", A, in methanol has absorption maxima at λ 244 $\text{m}\mu$ (ϵ 20800) and 324 $\text{m}\mu$ (ϵ 3200). The corresponding methyl derivative shows only one peak at 220 $\text{m}\mu$ (ϵ 23700) with shoulders at c. 248 and 294 $\text{m}\mu$.

Acknowledgments

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⁷ Busch, M., *Ber. dt. chem. Ges.*, 1895, **28**, 2635.