

THE ν -TRIAZOLO[5,1-c]-AS-TRIAZINE RING SYSTEM AND A SYNTHETIC ROUTE TO
NOVEL AS-TRIAZINE DERIVATIVES

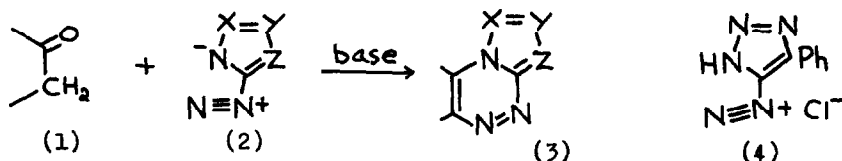
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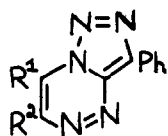
In contrast to their benzenoid counterparts, the reactions of five-membered heterocyclic diazonium salts¹ have been comparatively little studied. In particular, the potential bifunctional reactivity of the derived diazonium betaines (2) might provide the basis for a general route [(1) + (2) \rightarrow (3)] to fused as-triazines exemplified by the conversion of 1H-pyrazole diazonium salts into pyrazolo[5,1-c]-as-triazines.² The application of the annellation



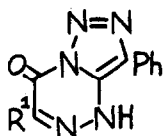
process [(1) + (2) \rightarrow (3)] to the synthesis of the hitherto unknown ν -triazolo [5,1-c]-as-triazine ring system is now described.[†] Acid-catalysed triazole scission³ of this ring system provides a valuable method for the synthesis of as-triazine derivatives[†] of a type which are otherwise obtainable only with difficulty and which are of potential value as synthetic intermediates (e.g. in azapteridine synthesis⁴).

Acetylacetone coupled with the diazonium salt (4) in aqueous ethanol at room temperature in the presence of sodium acetate to give 6-acetyl-7-methyl-3-phenyl- ν -triazolo[5,1-c]-as-triazine (5a) (90%), m.p. 210°, whose structure follows from its reaction with phenylhydrazine to give the azo-compound (8) thereby excluding the alternative structure (7), the product of a subsequent Dimroth rearrangement³ of (5a). The triazolotriazines (5b and c) were similarly obtained (80-90%) from the salt (4) and benzoylacetone or ethyl acetoacetate. Coupling of the salt (4) with diethyl malonate, ethyl

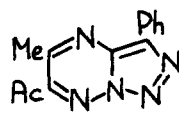
cyanoacetate, or cyanoacetamide gave mixtures of triazolotriazines (6a) and (5d and e) and the derived hydrazones (9a-c), whereas hydrazones (9d-f) were the sole products (60-90%) of the coupling reactions of benzoylacetonitrile, ethyl benzoylacetate, or dibenzoylmethane. Heated in aqueous ethanolic sodium acetate, the hydrazones (9a-e) afforded the corresponding triazolotriazines (6a) and (5d-g) (>90%). In the cyclisation of the hydrazone (9f) both possible products (5h) and (6b) were obtained. Heating the amino-amide (5e) under reflux (17h) in glacial acetic acid gave 3-(α-acetoxybenzyl)-5-amino-as-triazine-6-carboxamide (10d) (67%), m.p. 105°. The as-triazines (10a-c) were obtained similarly.



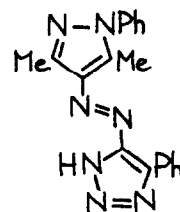
(5)	R ¹	R ²
a;	Me	Ac
b;	Me	Bz
c;	Me	CO ₂ E
d;	NH ₂	CO ₂ Et
e;	NH ₂	CONH ₂
f;	NH ₂	Bz
g;	Ph	Bz
h;	Ph	CO ₂ Et



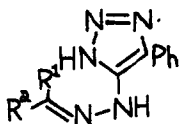
(6)	R ¹
a;	CO ₂ Et
b;	Bz



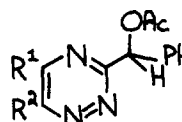
(7)



(8)



(9)	R ¹	R'
a;	CO ₂ Et	CO ₂ Et
b;	CN	CO ₂ Et
c;	CN	CONH ₂
d;	CN	Bz
e;	Bz	Bz
f;	Bz	CO ₂ Et



(10)	R ¹	R ²
a;	Me	Bz
b;	Ph	Bz
c;	NH ₂	CO ₂ Et
d;	NH ₂	CONH ₂

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 † Satisfactory analyses and spectral data were obtained for all new compounds

¹ J. M. Tedder, *Adv. Heterocyclic Chem.*, 1967, **8**, 1.

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³ D. R. Sutherland and G. Tennant, *J. Chem. Soc. (C)*, 1971, 2156.

⁴ E. C. Taylor and S. F. Martin, *J. Org. Chem.*, 1970, **35**, 3792;

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