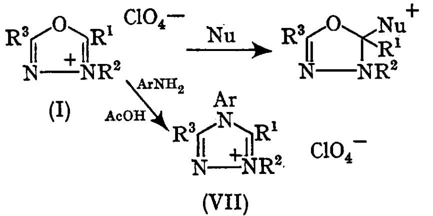
The Action of Nucleophilic Reagents on 1,3,4-Oxadiazolium Salts

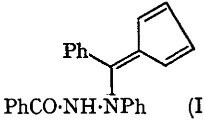
By G. V. BOYD* and A. J. H. SUMMERS

(*Department of Chemistry, Chelsea College of Science and Technology, London, S.W.3*)

THE ease with which 1,3,4-oxadiazolium salts (I) are hydrolysed to diacylhydrazines has been noted previously.[1] We find that these salts are attacked by many other nucleophiles (Nu) to yield a variety of novel compounds. These reactions involve the initial formation of an adduct (II) which may undergo further transformations. The adduct is isolated when the nucleophile is an alkoxide ion, *e.g.* 2,3,5-triphenyloxadiazolium perchlorate (I; $R^1 = R^2 = R^3 = Ph$) and sodium ethoxide yield 2-ethoxy-2,3,5-triphenyl-Δ^4-1,3,4-oxadiazoline (II; $R^1 = R^2 = R^3 = Ph$, $Nu = OEt^-$), m.p. 108—109°,† which reverts to the oxadiazolium salt on treatment with perchloric acid. If the nucleophile can lose a proton the primary adduct undergoes ring-opening; this is observed in the reactions with sodium cyclopentadienide, hydrogen sulphide, and ethanolic aniline, which with triphenyloxadiazolium perchlorate yield, respectively, the orange acylhydrazinofulvene (III), m.p. 190—191°, the yellow acylthioacylhydrazine (IV), m.p. 190—191°, and a salt whose infrared spectrum is consistent with the amidrazonium structure (V). Deprotonation of this salt with triethylamine gave the base (VI), m.p. 139—141°, while treatment with acetic acid caused ring closure to yield 1,3,4,5-tetraphenyl-1,2,4-triazolium perchlorate (VIIa), which was also formed quantitatively when the oxadiazolium salt was briefly heated with aniline in acetic acid. This appears to be the first reported 1,4-diaryl-1,2,4-triazolium salt lacking functional substituents.



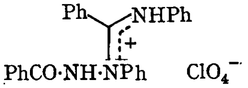
(I) (II) (VII)



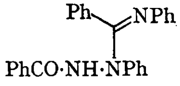
(III)

PhCO·NH·NPh·CSPh

(IV)



(V)



(VI)

The smooth formation of *s*-triazolium salts on heating 1,3,4-oxadiazolium salts with primary aromatic amines in acetic acid is quite general; the Table lists some of the triazolium salts prepared in this way. *s*-Triazoles are similarly obtained using ammonium acetate, *e.g.* triphenyloxadiazolium perchlorate gives the known 1,3,5-triphenyl-1,2,4-triazole.

s-*Triazolium perchlorates*

Formula (VII)

Compound	R^1	R^2	R^3	Ar	M.p. (°C)
(VIIa)..	Ph	Ph	Ph	Ph	> 330
(VIIb)..	Me	Ph	Me	Ph	196—197
(VIIc)..	Me	Ph	Me	o-Me·C_6H_4	153—154
(VIId)..	Me	Ph	Me	p-Me·C_6H_4	201—203
(VIIe)..	Me	Ph	Me	2,6-Me_2·C_6H_3	241—243
(VIIf)	Me	Ph	Me	m-NO_2·C_6H_4	228—229
(VIIg)..	Me	Ph	Me	p-NO_2·C_6H_4	201—202
(VIIh)..	Me	Ph	Me	m-HO_2C·C_6H_4	250 (decomp.)
(VIIi)	Me	Ph	Ph	Ph	227—228
(VIIj)	Me	Ph	Ph	p-Me·C_6H_4	244
(VIIk)..	Me	Ph	Ph	p-HO·C_6H_4	218—220
(VIIl)	Me	Me	Ph	Ph	168—169

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† Satisfactory analytical and spectroscopic data have been obtained for all new compounds whose melting points are given.

[1] G. V. Boyd, *Chem. Comm.*, 1967, 954.