1,3,4-Oxadiazolium Salts

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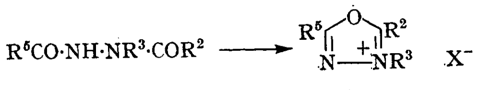
No quaternary salts derived from simple 1,3,4-oxadiazoles appear to have been described, whereas *N*-alkyl-1,2,4- and 1,2,5-oxadiazolium salts are known.[1] It has now been found that 1,3,4-oxadiazoles can be protonated and alkylated and stable salts, *e.g.*, (Ia–d, Iq) (see Table), are easily obtained.

3-Aryl-1,3,4-oxadiazolium perchlorates (I; R^3 = aryl, X = ClO_4) are formed in excellent yields when 1,2-diacyl-1-arylhydrazines are treated with 70% perchloric acid in acetic anhydride:



(I)

The general method can be modified in various ways: (i) 3-aryl-2-methyl-1,3,4-oxadiazolium perchlorates are obtained from 2-acyl-1-arylhydrazines and acetic anhydride–perchloric acid, thus the salts (Ig) and (Ii) were made from 2-formyl- and 2-benzoyl-1-phenylhydrazine, respectively; (ii) 3-aryl-2,5-dimethyloxadiazolium perchlorates, *e.g.* compounds (Ih) and (In), are formed directly from arylhydrazines and acetic anhydride–perchloric acid; (iii) other acid anhydrides may be used in place of acetic anhydride, thus treatment of 2-benzoyl-1-phenylhydrazine and of *p*-nitrophenylhydrazine with propionic anhydride–perchloric acid gave the ethyloxadiazolium salts, (Io) and (Ip), respectively; (iv) tetrafluoroborates, *e.g.*, compounds (Ij) and (Im), were prepared by substituting 40% tetrafluoroboric acid for perchloric acid. Furthermore, the method can be extended to the synthesis of 1,3,4-oxadiazoles: 1,2-diacylhydrazines on treatment with acid anhydrides and perchloric acid afford 3*H*- or 4*H*-1,3,4-oxadiazolium perchlorates which are readily deprotonated to oxadiazoles, *e.g.*, 1,2-dibenzoylhydrazine gave the salt (Ia) and thence 2,5-diphenyl-1,3,4-oxadiazole, benzhydrazide reacted with acetic anhydride–perchloric acid to give compound (Ib) which yielded 2-methyl-5-phenyloxadiazole quantitatively when stirred with water, similarly from *p*-nitrobenzhydrazide, propionic anhydride, and perchloric acid, the salt (Iq) and thence the known 2-ethyl-5-*p*-nitrophenyl-1,3,4-oxadiazole were obtained.

The Table lists some of the oxadiazolium salts prepared. Correct analyses were obtained for all compounds, their structures are substantiated by

TABLE

1,3,4-*Oxadiazolium salts*

Compound	Formula (I) R^2	R^3	R^5	X	Yield (%)	M.p.	Chemical shift of *C*-methyl protons (τ) in CF_3·CO_2H
(Ia)	Ph	H	Ph	ClO_4	31	249°	—
(Ib)	Me	H	Ph	ClO_4	92	184	6·96
(Ic)	Me	Me	Ph	ClO_4	82	229[a]	6·91
(Id)	Me	Et	Ph	BF_4	84	152·5	6·91
(Ie)	H	Ph	H	ClO_4	81	135[a,b]	—
(If)	H	Ph	Me	ClO_4	87	140[a,b]	7·10
(Ig)	Me	Ph	H	ClO_4	55	216[a]	6·86
(Ih)	Me	Ph	Me	ClO_4	81	114[b]	6·96, 7·20
(Ii)	Me	Ph	Ph	ClO_4	94	189	6·87
(Ij)	Me	Ph	Ph	BF_4	95	163·5	6·87
(Ik)	Ph	Ph	Me	ClO_4	75	209·5	7·11
(Il)	Ph	Ph	Ph	ClO_4	97	272[a]	—
(Im)	Ph	Ph	Ph	BF_4	98	237[a]	—
(In)	Me	*p*-NO_2·C_6H_4	Me	ClO_4	95	219[a]	6·81, 7·12
(Io)	Et	Ph	Ph	ClO_4	95	197·5	—
(Ip)	Et	*p*-NO_2·C_6H_4	Et	ClO_4	75	161[a,b]	—
(Iq)	Et	H	*p*-NO_2·C_6H_4	ClO_4	85	200[a,c]	—

[a] With decomposition; [b] Hygroscopic; [c] Protonation on N-3 is probable.

the infrared spectra which are devoid of amide and hydroxyl bands but exhibit $C{=}N^+$ absorption at 1620—1630 cm.$^{-1}$ The n.m.r. spectra of the *C*-methyl salts are revealing: the protons of 2-methyl groups resonate at *ca.* τ 6·9, those of 5-methyl groups at 7·1—7·2. 2-Methyl-5-phenyl-1,3,4-oxadiazole on protonation, methylation, and ethylation yielded salts each of which showed a single methyl signal near τ 6·9, characteristic of a 2-methyl group. Attack must therefore have occurred at N-3 in each case and the salts are accordingly formulated as (Ib), (Ic), and (Id), respectively.

2-Alkyl groups in the oxadiazolium salts (I; R^3 = H, alkyl or aryl) are reactive; thus 2-methyl-3,5-diphenyloxadiazolium perchlorate (Ii) condenses with *p*-dimethylaminobenzaldehyde in boiling acetic acid to yield a red styryl derivative, the isomeric 5-methyl compound (Ik) does not react under these conditions.

The 3-aryloxadiazolium salts are very sensitive to nucleophilic attack. Treatment with water results in ring fission to yield diacylarylhydrazines. The action of other nucleophiles is under investigation.

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[1] R. A. Olofson and J. S. Michelman, *J. Amer. Chem. Soc.*, **1964**, **86**, 1863; J. S. Michelman, *Diss. Abs.*, 1965, **26**, 1920.