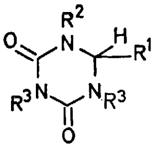
Chlorosulphonylisocyanate Addition to Anils: Formation of Triazinediones

By RALPH E. WALROND and HANS SUSCHITZKY*
(*Department of Chemistry and Applied Chemistry, University of Salford, Salford* M5 4WT, *Lancashire*)

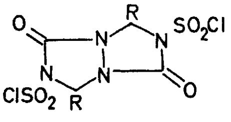
Summary The azomethine bond undergoes thermal (2+4) cycloaddition with 2 molecules of chlorosulphonylisocyanate to give *s*-triazinediones (**1**) in high yield.

CYCLOADDITION of chlorosulphonylisocyanate (CSI) with carbon–carbon multiple bonds is a well documented reaction of synthetic significance,[1] which proceeds almost invariably in a (2+2) manner. Interaction of CSI with a C=N– bond, however, has only been reported recently[2] in the case of a ketenimine (>C=C=N–) which gave an unstable diazinone.

As part of a general study of the reaction of CSI with >C=N– groups we found that solutions of anils in methylene chloride react at room temperature with 2 mol of CSI to give the novel *N*-chlorosulphonyl-*s*-triazinediones (**1**; $R^3 = SO_2Cl$) in high yield (*cf.* Table). These compounds are stable for several days even on exposure to air and light and are reductively converted (at pH 7—8 in $NaHSO_3$) into the corresponding *s*-triazinediones (**1**; $R^3 = H$; *cf.* Table). The structures are confirmed by analytical and spectral evidence. For instance, compound (**1a**) ($R^1 = R^2 = Ph$, $R^3 = SO_2Cl$) shows bands at 1770 and 1790 (>C=O) and at 1200 and 1370 cm^{-1} (SO_2). The n.m.r. spectrum shows peaks at τ 2·45 (10H), and at 2·95 (1H). A peak of *m/e* 365 (corresponding to $M^+ - SO_2Cl$) was observed. On reduction of compound (**1**; $R^1 = R^2 = Ph$, $R^3 = H$) coupling between NH and the adjacent >CH appears which is suppressed by deuterium oxide addition. M.s. data clearly showed a molecular ion peak. All other compounds were similarly identified. Only in the case of a *p*-NO_2-group (**1g**) did the method fail, possibly because of deactivation of the anil towards cycloaddition.



(1)



(2)

TABLE. *Triazinediones* (**1**) *from CSI and Schiff's bases*

	R^1	R^2	$R^3 = SO_2Cl$ % yield	$R^3 = SO_2Cl$ m.p. (°C)	$R^3 = H$ % yield	$R^3 = H$ m.p. (°C)
a	Ph	Ph	100	95	95	256
b	*p*-$MeOC_6H_4$	Ph	86	140	—	250
c	*p*-ClC_6H_4	Ph	73	110	60	270
d	*p*-$NO_2C_6H_4$	Ph	50	140	40	248
e	Ph	*p*-$MeOC_6H_4$	50	104	95	256
f	Ph	*p*-ClC_6H_4	60	122	80	260
g	Ph	*p*-$NO_2C_6H_4$	0	—	—	—
h	Ph	*m*-$NO_2C_6H_4$	78	145	95	260
i	Ph	*o*-ClC_6H_4	50	110	90	192
j	Ph	$PhCH_2$	60	120	60	260
k	Ph	C_6H_{11}	65	110	65	280

[a] All new compounds had the expected analytical and spectral data.

The full scope of this (2+4) cycloaddition involving a C=N– moiety which may, however, be preceded by a (2+2) cycloaddition in which a dipolar intermediate is formed from the anil and the reagent (CSI), is being studied.

One extension involves azines $(RCH=N–)_2$ which predictably reacted with CSI to give the triazoles (**2**; R = Ph or $MeOC_6H_4$) analogous to the reported interaction with arylisocyanates.[3]

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[3] J. R. Bailey and A. T. McPherson, *J. Amer. Chem. Soc.*, 1917, **39**, 1322.