Nucleophilic Substitution of 1-Chloro-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazene 1,3,5-Trioxide (Diphenylsulphanuric Chloride) by Secondary Amines

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Summary 1-Chloro-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazene 1,3,5-trioxide (diphenylsulphanuric chloride) undergoes nucleophilic substitution with secondary amines without ring-cleavage to give diphenyl sulphanuric amides, a new class of stable compounds, in good yields.

Reactions of α (*cis*) sulphanuric chloride $(NSOCl)_3$, with nucleophiles normally results in ring cleavage,[1] with the exception of weaker nucleophiles like morpholine (under controlled conditions)[2] and diphenylmercury.[3] Furthermore, diphenylsulphanuric chloride (1-chloro-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-trioxide)[4] (**1**) is reported to give no isolated substitution products with an excess of diphenylmercury,[3] phenyl-lithium,[3] or potassium thiocyanate.[5]

Contrary to the implications of previous work,[3,5] we have shown that (**1**) reacts readily with secondary amines in benzene or acetonitrile to give diphenylsulphanuric amides (1-dialkylamino-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-trioxides) (**2**) in 45—80% yields.

Treatment of a *ca.* 0·03 M benzene solution of (**1**) with morpholine, at room temperature, resulted in the precipitation of a white solid which was filtered off, washed with cold water, and crystallized from ethanol–hexane to give (**2a**).† Piperidine and diethylamine also reacted with (**1**) to give

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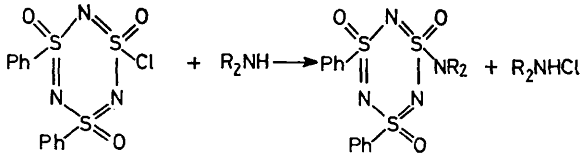
† All new compounds gave satisfactory elemental analyses and i.r. and n.m.r. spectra.

TABLE

Amine	Product	Solvent	Reaction time/h [(**1**) : Amine] (1 : 3)	(1 : 6)	Yield/%[a]	M.p./°C
Morpholine	(**2a**)	C_6H_6	8·5	2·0	76	140—141
,,	,,	MeCN	115	2·5	65	,,
Piperidine	(**2b**)	C_6H_6	0·5	0·25	80	151·5—152·5
,,	,,	MeCN	106	2·2	78	,,
Diethylamine	(**2c**)	C_6H_6	1·4	0·2	67	127—128
,,	,,	MeCN	36	2·3	45	,,
,,	,,	,,	—	1·5[b]		

[a] Yields are reported for reactions with a ratio of (**1**) : amine of 1 : 6. [b] Reaction time with (**1**), $NHEt_2$, and Et_4NCl in the ratio of 1 : 6 : 6.



(1) (2)

(**2b**) and (**2c**), respectively. Treatment of an acetonitrile solution of (**1**) with the above amines gave the same products.‡

As shown in the Table, the structure and the concentration of the amines had a marked influence on the progress of the reaction.§ Piperidine and diethylamine, which are more nucleophilic than morpholine, reacted at a much faster rate. Doubling the concentration of amine also increased the rate. For example, the reaction of (**1**) with morpholine in benzene in a ratio of 1 : 3 required 8·5 h compared with 2 h for a 1 : 6 ratio. Reaction times were shorter in benzene than in acetonitrile, apparently because the products precipitated from benzene. These results and the observation that the reaction time for (**1**) with diethylamine in the presence of Et_4NCl (common ion) did not decrease, suggest that substitution occurs in S_N2 fashion.

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‡ Earlier (172nd A.C.S. National Meeting, San Francisco, Aug. 29—Sept. 3, 1976), we reported that (**1**) failed to react with amines when benzene was used as a solvent. However, subsequent experiments showed otherwise.

§ The progress of the reaction was monitored by t.l.c. on silica gel strips (Eastman Kodak) eluted with benzene and was judged complete when the spot corresponding to (**1**) (R_f 0·83) had disappeared completely.

[1] T. Moeller and R. L. Dieck in 'Preparative Inorganic Reactions,' vol. 6, ed. W. L. Jolly, Wiley–Interscience, New York, 1971, p. 63.
[2] A. Failli, M. A. Kresge, C. W. Allen, and T. Moeller, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 165.
[3] R. L. McKenney, Jr., and N. R. Fetter, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2927.
[4] β-Sulphanuric chloride gives the same isomer of (**1**) as α; T. J. Maricich and M. H. Khalil, unpublished results.
[5] A. J. Banister and B. Bell, *J. Chem. Soc.* (*A*), 1970, 1659.