

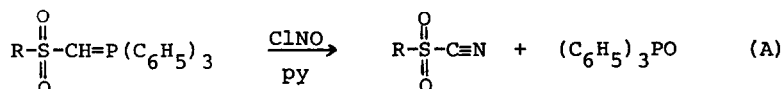
NUCLEOPHILIC DISPLACEMENTS ON SULFONYL CYANIDES (1)

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(Received in UK 26 January 1970; accepted for publication 5 February 1970)

Sulfonyl cyanides have been synthesized recently in this laboratory (2) according to



Shortly afterwards, two other syntheses were published. One by Cox and Ghosh (3), who have prepared several alkyl and aryl sulfonyl cyanides from sulfinates and cyanogen chloride.



Most recently, Pews and Corson (4) reported two sulfonyl cyanides obtained by oxidation of thiocyanates with *m*-chloroperbenzoic acid.

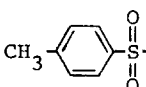


Thus, within two years three different synthetic approaches to this new class of compounds have been disclosed. Of these, reaction B seems the method of choice, both with respect to the yields and the ease of performance.

We now wish to report the behaviour of *p*-toluenesulfonyl cyanide (tosyl cyanide) towards various nucleophiles. These reactions are of interest, since a priori two sites are conceivable for nucleophilic attack: (i) the cyano carbon, and (ii) the sulfone sulfur. The SO₂ group in tosyl cyanide probably will reduce inductively the electron density at the cyano carbon (as compared with aryl or alkyl cyanides). Therefore, enhanced reactivity of the cyano group with

nucleophiles might be expected. Also possible, but less likely, seems the reverse in which nucleophilic attack is directed towards the sulfur atom by the electronwithdrawing cyano group.

With lithium phenoxide, with sodium p-thiocresolate and with diethylamine the cyano group is transferred from tosyl cyanide to the nucleophile in a smooth reaction (see Table).

Reactions of  with nucleophilic reagents

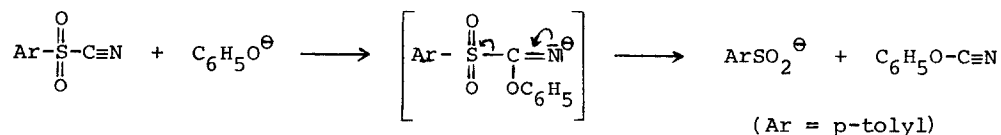
Nucleophile	Solvent	Conditions	Products ^{a)}	Yield
C ₆ H ₅ OLi	benzene	15 min (5°)	C ₆ H ₅ OC≡N	40%
p-CH ₃ C ₆ H ₄ SNa	ethanol	15 min (20°)	p-CH ₃ C ₆ H ₄ SC≡N	65%
C ₆ H ₅ MgBr	ether	30 min (20°)	C ₆ H ₅ C≡N (ref. 2)	40%
p-CH ₃ C ₆ H ₄ SO ₂ CH=PPh ₃	benzene	6 hrs (80°)	p-CH ₃ C ₆ H ₄ SO ₂ -C≡N C=PPh ₃ ^{b)}	50%
(C ₂ H ₅) ₂ NH	CH ₂ Cl ₂	15 min (20°)	(C ₂ H ₅) ₂ NC≡N	70%
p-CH ₃ C ₆ H ₄ SH	CH ₂ Cl ₂	15 min (20°)	p-CH ₃ C ₆ H ₄ SC≡N ^{c)}	41%
C ₆ H ₅ SH	CH ₂ Cl ₂	15 min (20°)	C ₆ H ₅ SC≡N ^{c)}	48%
CH ₃ CH ₂ CH ₂ SH	neat	30 min (70°)	CH ₃ CH ₂ CH ₂ SC≡N ^{c)}	56%
P(C ₆ H ₅) ₃	benzene	1.5 hrs (80°)	{ p-CH ₃ C ₆ H ₄ SC≡N (C ₆ H ₅) ₃ PO	{ 87% 98%

a) All known products are identified by comparison with authentic samples.

b) M.p. 223-224°; elemental analysis and spectral data support this structure.

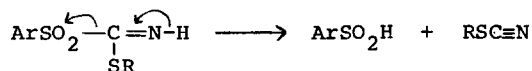
c) In the reactions with RSH other products have been detected in various amounts: ArSO₂SAr, ArSO₂SR, ArSSR, RSSR and RSCONH₂ (Ar = p-tolyl).

These results are explained by an addition-elimination process, e.g.



The less strongly nucleophilic tosylmethylenetriphenylphosphorane requires more drastic reaction conditions (6 hrs at 80°) to form the corresponding cyano ylid, a compound not reported previously.

The reactions with thiols (see Table) are described adequately by an addition-elimination process, through



The results of hydrolysis of tosyl cyanide also indicate enhanced reactivity of the cyano group as discussed above. A 0.05 molar solution of tosyl cyanide in 2 N aqueous NaOH-dioxan (1:1) is completely hydrolysed within one hour at room temperature, whereas under neutral conditions (water-dioxan 1:1) tosyl cyanide (0.05 molar) is converted with a half-life of about 6 hrs (5). p-Toluene-sulfonic acid (salt) is formed in both reactions (replace $\text{C}_6\text{H}_5\text{O}^\ominus$ by OH^\ominus , RSH by H_2O in Schemes above) and isolated, after reaction with CH_3I , as methyl p-tolyl sulfone (yield 73%, resp. 62%).

Apparently, tosyl cyanide belongs to the category of cyanides with an activated cyano group, like cyanates and thiocyanates (6) and cyanogen halides⁻ (7). The reaction of nucleophiles with tosyl cyanide is in contrast, however, with acyl cyanides ($\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}\equiv\text{N}$) where the carbonyl group is attacked (8).

The reaction of tosyl cyanide with triphenylphosphine takes a different course. No transfer of $\text{C}\equiv\text{N}$ is observed, but instead the sulfonyl group is reduced to give p-tolylthiocyanate.

ACKNOWLEDGMENT

The authors are much indebted to Prof. Dr. J. Strating for his stimulating interest.

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Further examples of $\text{RSO}_2\text{C}\equiv\text{N}$, obtained by this method, are $\text{R} = \text{C}_6\text{H}_5$ (40%, b.p. 103/1 mm), $\text{p-ClC}_6\text{H}_4$ (41%, m.p. 56-58°), $\text{C}_6\text{H}_5\text{CH}_2$ (50%, m.p. 85-87°).
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4. R. G. Pews and F. P. Corson, Chem. Comm., 1969, 1187; $\text{R} = \text{p-CH}_3\text{C}_6\text{H}_4$ (79%) and $\text{R} = \text{C}_2\text{H}_5$ (6%). We have discovered the same reaction independently, using *m*-chloroperbenzoic acid in refluxing carbon tetrachloride. Thus were obtained the following sulfonyl cyanides: $\text{R} = \text{C}_6\text{H}_5$ (43%); 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2$ (22%, m.p. 39-41°); $\text{C}_6\text{H}_5\text{CH}_2$ (4%, m.p. 84-86°); $\text{CH}_3\text{CH}_2\text{CH}_2$ (11%, b.p. ca. 50°/0.5 mm), A. M. van Leusen and H. J. Witting, unpublished results.
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