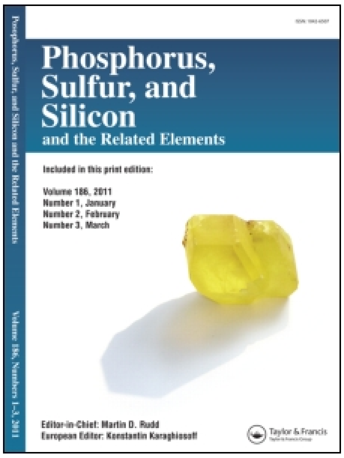

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STEREOSELECTIVE SYNTHESIS OF (2Z)-α,β-UNSATURATED NITRILES VIA TANDEM CONDENSATION-DESULFONYLATION OF α-CYANOSULFONES WITH ALDEHYDES

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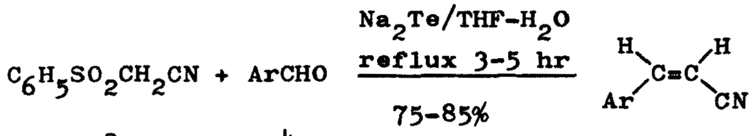
Abstract In the presence of sodium telluride, α-cyanosulfones undergo tandem condensation-desulfonylation reaction with aromatic aldehydes to give (2Z)-α,β-unsaturated nitriles with good stereoselectivity.

α-Cyano-α,β-unsaturated sulfones can be easily prepared through the condensation of α-cyanosulfones with aldehydes[1,2]. It was reported that they can be desulfonylated by electrochemical reduction to give nitriles[3] and be selectively reduced the carbon-carbon double bond by formic acid in triethylamine-dimethylformamide to give α-cyanosulfones[4].

Recently, we found that sodium hydrogen telluride is both selective reducing agent and desulfonylating agent of α,β-unsaturated compounds[5,6,7]. Continuing this work, we study the reactivity of α-cyano-α,β-unsaturated sulfones acted by sodium hydrogen telluride. The experiment results show that, reacting α-cyano-α,β-unsaturated sulfones with sodium hydrogen telluride, desulfonylation was taken place preferentially and the C=C bond wasn't affected (method A).



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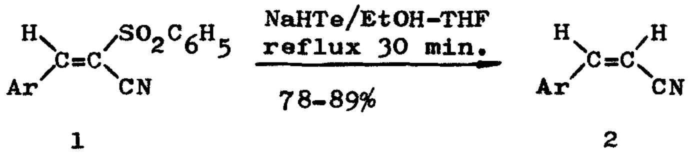
The above reaction has excellent stereoselectivity, which forms Z-isomers preferentially, no or little E-isomers were detected. This method also has the advantages of convenient operations, mild conditions, good yields and that tellurium can be retrieved to utilize.

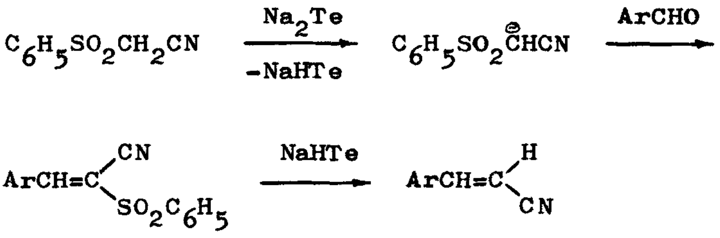
TABLE 1 Synthesis of (2Z)-α,β-unsaturated nitriles

Product	Ar	Yield (%) Method A	Yield (%) Method B
2a	C_6H_5	87	82
2b	$4-CH_3OC_6H_4$	84	80
2c	$4-ClC_6H_4$	85	79
2d	$2-ClC_6H_4$	78	75
2e	$3-ClC_6H_4$	80	76
2f	$4-BrC_6H_4$	87	80
2g	$3-BrC_6H_4$	80	77
2h	$4-(CH_3)_2NC_6H_4$	89	85



This reductive desulfonylation has excellent stereoselectivity. Starting from (2E)-α-cyano-α,β-unsaturated sulfones 1, desulfonylation affords almost 100% Z-isomer of α ,β-unsaturated nitriles, which can't prepared by Wittig reaction or condensation.

Considering that sodium telluride is also a alkaline reagent, we may expect that it cause α-cyanosulfones to undergo condensation with aromatic aldehydes to give α-cyano-α,β-unsaturated sulfones and itself can form sodium hydrogen telluride at the same time. Since sodium hydrogen telluride can react with α-cyano-α,β-unsaturated sulfones to desulfonylate, we think that the tandem reaction of condensation and desulfonylation of which starts from reacting α-cyanosulfones with aromatic aldehydes, can take place in one-pot reaction in the presence of sodium telluride.



The experiment results showed that α-cyanosulfones can undergo one-pot reaction with aromatic aldehydes to give α ,β-unsaturated nitriles in the presence of sodium telluride (method B).

TABLE 2 Melting points and spectral data of the products

Product	mp(°C)[a]	Lit.bp/torr or mp(°C)	IR(KBr)[c] (cm^{-1})	^{1}H-NMR(CDCl$_3$/TMS)[d] δ, J(Hz)
2a	oil	105-106°/10[8]	2205 1620	5.20(d,1H,J=12);6.69 (d,1H,J=12);6.75-7.72 (m,5H).
2b	oil	125-127°/2[9]	2215 1640	3.87(s,3H);5.30(d,1H, J=12);7.10(d,1H,J=12); 6.93-7.81(m,4H).
2c	63-65°	66.5-67.5°[8]	2210 1620	5.40(d,1H,J=12);7.12 (d,1H,J=12);6.70-7.72 (m,4H).
2d	oil	90-92°/1.2[8]	2220 1635	5.48(d,1H,J=12);7.31 (d,1H,J=12);6.78-7.75 (m,4H).
2e	oil	26-28°[10]	2215 1640	5.40(d,1H,J=12);7.12 (d,1H,J=12);6.40-7.73 (m,4H).
2f	69-71	69-69.5°[8]	2220 1635	5.41(d,1H,J=12);7.08 (d,1H,J=12);6.93-7.75 (m,4H).
2g	oil	C_9H_6BrN[b]	2220 1640	5.45(d,1H,J=12);7.10 (d,1H,J=12);7.01-7.71 (m,4H).
2h	59-61	60-61°[9]	2220 1635	3.01(s,3H);5.15(d,1H, J=12);7.01(d,1H,J=12); 6.63-7.74(m,4H).

[a] Uncorrected.

[b] Satisfactory microanalyses obtained: Found: C,52.34;H,2.67; N,6.95. Caclcd.: C,51.96;H,2.91;N,6.73.

[c] Recorded on Perkin Elmer 683 spectrophotometer.

[d] Recorded on JEOL FX 90Q spectrometer.

Synthesis of (2Z)-p-Chlorocinnamonitrile (2c); Typical Procedure:

Method A : To a solution of NaHTe, prepared from Te (1.3 g, 10mmol), $NaBH_4$ (0.9 g, 24 mmol) in EtOH (20 mL), under N_2 atmosphere, is added a solution of (2E)-α-cyano-β-(p-chlorophenyl)ethenyl phenyl sulfone (1c; 3.1 g, 10 mmol) in THF (20 mL), and the mixture is stirred at reflux for 30 minutes. The reaction is quenched with water (20 mL), and the mixture is filtered and the filtrate is extracted with chloroform (3x20 mL). The combined organic phase is dried by anhydrous magnesium sulfate and concentrated to give the crude product 2c, which is purified by column chromatography on silica gel using benzene as eluant; yield: 1.40 g (85%); mp 63-65°C (Lit.[8] 66.5-67.5°C).

Method B : To a solution of Na_2Te, prepared by heating a mixture of Te (1.30 g, 10 mml), $NaBH_4$ (0.9 g, 24 mmol) and water (10 mL) at 60-70°C under N_2 atmosphere, is added a solution of α-cyanomethyl phenyl sulfone (3, 1.81 g, 10 mmol) and p-chlorophenyl aldehyde (4c, 1.8 g, 12 mmol) in THF (20 mL). An instaneous reaction occured and the color of the reaction mixture changed from colorless to violet. The end of the reaction is detected by TLC (silica GF, benzene as eluant). The remaining work is analogous to method A and give 2c; yield: 1.3 g (79%); mp 63-65°C (Lit.[8] 66.5-57.5°C).

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