featureless and the g value of 2.0059 is consistent with spins partially localized at the sulfur atoms.

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1, 134177-77-8; **2**, 134177-78-9; **4**, 134177-79-0; **5**, 134177-80-3; 1,3-cyclopentanedione, 3859-41-4; 4,5-dimethyl-2-methylthio-1,3-dithiolium iodide, 105580-73-2.

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[19] a) X-ray structure analysis of **2**: $C_{10}H_8S_4$; $M_r = 258.45$; monoclinic space group $P2_1/n$; $a = 7.634(3)$, $b = 14.018(3)$ Å; $c = 10.561(3)$ Å; $\beta = 96.53(3)°$, $V = 1122.84$ Å^3; $Z = 4$; $\mu = 7.7$ cm^{-1}; $\varrho_{calcd} = 1.53$ g cm^{-3}; $T = 297$ K; $\lambda(Mo_{K\alpha}) = 0.71069$; $R = 0.056$; $R_w = 0.048$ for 3665 unique observed reflections. b) Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallography Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (UK), on quoting the full journal citation.
[20] Data are relative to Ag/AgCl, platinum electrode, compound **4** (ca. 1×10^{-5} M) with electrolyte tetraethylammonium hexafluorophosphate (0.01 M) in dry dichlormethane under argon, 20°C, initial reductive scan, rate 100 mVs^{-1}, using a BAS 100 Electrochemical Analyser. The C.V. was unchanged after continuous cycling for 0.5 h between 1.0 and 0.0 V. We note that the redox potentials of compound **4** are similar to those of tetrathiafulvalene ($E_1^{1/2} = +0.34$, $E_2^{1/2} = +0.78$ V measured under identical conditions) and we are, therefore, pursuing the possibility of forming organic conductors based on system **4**.
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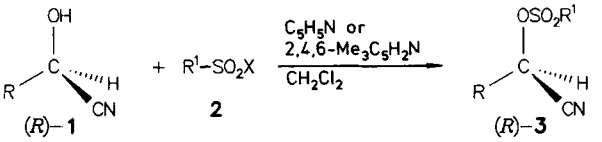
Synthesis and Stereoselective Reactions of (*R*)-α-Sulfonyloxynitriles**

By *Franz Effenberger** and *Uwe Stelzer*

Dedicated to Professor Hans Georg von Schnering on the occasion of his 60th birthday

(*R*)- and (*S*)-cyanohydrins are accessible via the enzyme-catalyzed addition of hydrocyanic acid to aldehydes.[1] They are useful, inter alia, for the production of enantiomerically pure α-hydroxycarboxylic acids[1c, 2] and β-aminoalcohols.[1a, 2] We report here on an important extension of the synthetic potential of optically active cyanohydrins by conversion of the hydroxy group into a good leaving group. Of particular interest are reactions of the cyanohydrin derivatives in which the nitrogen of the cyano group remains in the molecule, since compounds of this type are not directly accessible via α-amino- or α-hydroxycarboxylic acids.

Whereas stereoselective nucleophilic substitution in the α-position of carboxylic acids and carboxylates presents few difficulties,[3] very little is known about a corresponding reaction of α-substituted nitriles.[4] Starting from optically active nitriles with a leaving group in the α-position, only α-halonitriles have so far been prepared,[4] but these readily racemize in the presence of halide ions liberated in substitution reactions.[4a] Optically active α-sulfonyloxynitriles, which should be considerably more stable configurationally on account of the less nucleophilic sulfonate leaving groups,[3] have so far not been described. By reaction of the optically active cyanohydrins (*R*)-**1** as starting compounds with the sulfonyl halides and anhydrides **2**, we have now been able to synthesize aliphatic and aromatic (*R*)-α-sulfonyloxynitriles (*R*)-**3** free of racemization and in good yields.



X = Hal, OSO_2R^1

R	R^1
Alkyl, Cyclohexyl	4-$CH_3C_6H_4$, CH_3, CF_3
Aryl	CH_3, CF_3

With aliphatic cyanohydrins the tosylates and methane- and trifluoromethanesulfonates were synthesized in pure form. In the case of aromatic cyanohydrins, however, the preparation of mesylates is possible, but trifluoromethanesulfonates could only be synthesized and allowed to react in situ. These findings are consistent with data given in the literature on racemic cyanohydrin sulfonates, according to which the aliphatic compounds can be distilled without decomposition, whereas, e.g., the tosylate of mandelic nitrile already decomposes at room temperature.[5]

So far, it has not been possible to develop a suitable method for the direct determination of the optical purity of the compounds (*R*)-**3**. No information about the enantiomeric excesses can be gleaned from the experimentally determined rotation values, which lie between + 20° and + 60°, because of a lack of data for comparison. That the sulfonylations of (*R*)-**1** leading to (*R*)-**3** proceed without racemization could be demonstrated by the reactions of the α-sulfonyloxynitriles (*R*)-**3** with nucleophiles outlined in Scheme 1. According to Scheme 1, the cyanohydrin derivatives (*S*)-**4**, α-(phthaloylamino)nitriles (*S*)-**5**, α-azidonitriles (*S*)-**6**, and aziridines (*S*)-**7** are readily accessible in optically active form from the compounds (*R*)-**3**.

The reactions (b) and (c) have so far only been carried out with the aliphatic α-sulfonyloxynitriles (*R*)-**3**, the reactions (a) and (d) with both aliphatic as well as aromatic α-sulfonyloxynitriles (*R*)-**3**. Already at room temperature the reaction of (*R*)-**3a** with potassium acetate leads in very good yields to the cyanohydrin acetate (*S*)-**4a**, the enantiomeric purity of which was estimated by comparative investigations[6] to be 96.1% *ee*. Since the (*R*)-**1a** employed had an enantiomeric

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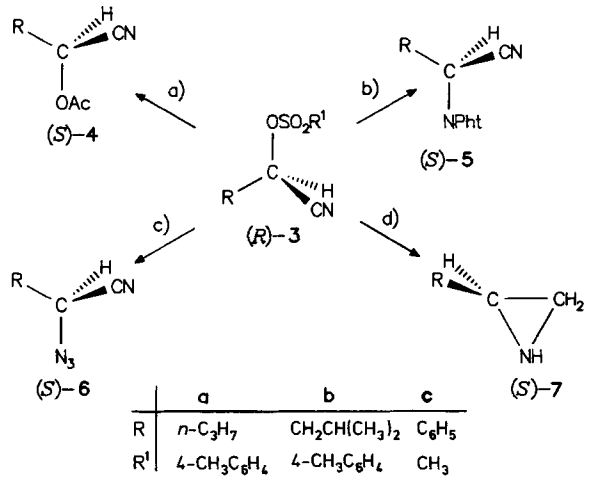

Scheme 1. a) (*R*)-**3a** + 1.5 mol CH_3CO_2K in dimethylformamide (DMF), 79 h, 20 °C; 84% (*S*)-**4a** (*ee* = 96%). b) (*R*)-**3a** + 1.5 mol potassium phthalimide in DMF, 6 d, 20 °C; 70% (*S*)-**5a** (*ee* = 93%). Pht = phthaloyl. c) (*R*)-**3b** + 1.5 mol KN_3 in DMF, 3 d, 20 °C; 78% (*S*)-**6b** ($[\alpha]_D^{20} = -36.1°$ (*c* = 0.77, CH_2Cl_2)). d) A solution of (*R*)-**3b** in Et_2O was added dropwise to a solution of $LiAlH_4$ in Et_2O at −80 °C; after warming to room temperature within 2 h the mixture was neutralized at −70 °C with K_2HPO_4/KH_2PO_4 buffer (pH 7); 64% (*S*)-**7b** ($[\alpha]_D^{20} = -16.8°$ (*c* = 5.39, EtOH)). (*R*)-**3c** was allowed to react under the same conditions; 56% (*S*)-**7c** ($[\alpha]_D^{20} = +31.7°$ (*c* = 2.59, $CHCl_3$)).

purity of 96.3% *ee*, it must be concluded that the conversion of (*R*)-**1a** into (*R*)-**3a** proceeds almost free of racemization and the nucleophilic substitution of (*R*)-**3a** leading to (*S*)-**4a** solely involves an S_N2-mechanism. Since aliphatic (*S*)-cyanohydrins, in contrast to the (*R*)-cyanohydrins, are not accessible via the enzyme-catalyzed addition of hydrocyanic acid to aldehydes,[1c] this route provides a valuable extension to the synthesis of aliphatic (*S*)-cyanohydrins.

The reactions with potassium phthalimide leading to *N*-phthaloyl-protected α-aminonitriles (*S*)-**5**[7] and with potassium azide leading to the α-azidonitriles (*S*)-**6** also take place at room temperature. α-Azidonitriles have thus far not yet been described in the literature, neither as (*R*)- nor as (*S*)-enantiomers. That the substitutions of (*R*)-**3b** to give (*S*)-**6b** also proceed stereoselectively, was confirmed by hydrogenation of (*S*)-**6b** in the known (2*S*)-1,2-diamino-4-methylpentane.[8] The enantiomeric excess in (*S*)-**5a** was determined with NMR-shift reagents to be 93% *ee*.

Aziridines[9] are of equally great importance as intermediates in synthesis as oxiranes. The ready accessibility of the compounds (*R*)-**3** opened up the possibility of preparing optically active aziridines (*S*)-**7** in a simple way by the method of *Ohta* et al.,[4b] via hydrogenation of the cyano group with $LiAlH_4$, followed by intramolecular substitution. The optical purity of the compounds (*S*)-**7b** and (*S*)-**7c** obtained were determined by comparison of their rotation values with data quoted in the literature,[10] though in the hydrogenation of (*R*)-**3c** there arises the problem that difficultly separable 2-phenylethylamine is formed as by-product.

α-Sulfonyloxynitriles (*R*)-**3** show a pronounced dependence on structure in nucleophilic substitutions: the aliphatic compounds react with potassium acetate and other nucleophiles exclusively with inversion of configuration, the aromatic compounds, on the other hand, generally with racemization. Partial Walden inversion is found also upon reaction of the aromatic compounds with cesium acetate but only when trifluoromethanesulfonates are employed. A favoring of the S_N2-reaction is also observed in the case of the aromatic compounds by way of an intramolecular reaction with formation of a three-membered ring, as follows from the reaction of (*R*)-**3c**, which gives (*S*)-**7c** in good optical yields. An explanation for this reaction behavior of the α-sulfonyloxynitriles of aromatic cyanohydrins could possibly be the additional stabilization of the benzyl cations by the nitrile group in the α-position.[11]

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Ligand-Stabilized Bimetallic Colloids Identified by HRTEM and EDX**

By *Günter Schmid*,* *Andreas Lehnert*, *Jan-Olle Malm*, and *Jan-Olov Bovin*

Dedicated to Professor Hans-Georg von Schnering on the occasion of his 60th birthday

Bimetallic clusters and colloids are of special interest for two reasons. Firstly, they may serve as models for studying the formation of different alloys. Secondly, it is possible to save precious metal, like Pt, by optimizing the synthetic conditions so that only very thin surface layers occur.

Miner et al.[1] described the synthesis of gold–platinum and palladium–platinum alloys as monodisperse sols by

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[**] *G. S.* and *A. L.* are grateful to the Fonds der Chemischen Industrie for financial support. *J.-O. B* and *J.-O. M.* thank the Swedish Natural Science Research Council and the Swedish National Energy Administration. HRTEM = high-resolution transmission electron microscopy; EDX = energy disperse X-ray microanalysis.