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Reaction of Bis(dimethylglyoximato)(pyridine)styrylcobalt(III) Derivatives with Arenesulfenyl Chloride

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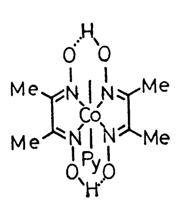
Synopsis. *cis*-Styryl and *trans*-styryl-type cobaloximes, having a *para*-substituent on the styrene moiety, give the corresponding *cis*- and *trans*-(styrylthio)benzene derivatives in excellent yields by the reaction with 2,4-dinitrobenzenesulfenyl chloride. The substitution proceeds stereospecifically with retention of configuration except for the case of *cis*-(*p*-cyanostyryl)cobaloxime.

Bis(dimethylglyoximato)(pyridine)cobalt(III) derivatives (the conventional name styryl-type cobaloxime is used hereafter) are converted to styryl-type halides and mercurials by reaction with bromine and mercury(II) acetate, respectively. The substitution proceeds stereospecifically with retention of configuration.[1,2] In this report the substitution of styryl-type cobaloximes with 2,4-dinitrobenzenesulfenyl chloride will be discussed. The reaction gives styryl-type sulfides, which may be utilized as a synthetic intermediate.[3] This reaction is an addition to the new synthetic routes for sulfides,[4–8] and the preparation of styryl-type cobaloxime is relatively simple.

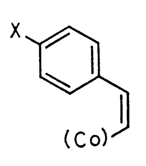
cis- and *trans*-Styryl-type cobaloximes (**1, 2,** and **3**) were synthesized from the corresponding styryl-type halides and the cobaloxime anion prepared *in situ* from dimethylglyoxime, pyridine, cobalt(II) chloride, and sodium borohydride.[1] Treatment of one of the *cis*-(**1c, 2c,** and **3c**) or *trans*-styryl-cobaloximes (**1t, 2t,** and **3t**) with 2,4-dinitrobenzenesulfenyl chloride in dichloromethane gave *cis*- (**4c, 5c,** and **6c**) and *trans*-2,4-dinitro-1-(styrylthio)benzene (**4t, 5t,** and **6t**), respectively, in excellent yields (see Table 1). The structures of the products were detected by elemental analyses and spectroscopy. The stereochemistry of the products was readily assigned by the coupling constants of vinyl hydrogens in the NMR spectra ($J=11$ Hz for *cis*-isomers and $J=16$ Hz for *trans*-isomers). The displacement of the cobaloxime moiety with 2,4-dinitrobenzenesulfenyl group proceeds with retention except in the reaction of *cis*-(*p*-cyanostyryl)cobaloxime (**1c**), in which a mixtures of *cis*- and *trans*-2,4-dinitro-1-(*p*-cyanostyrylthio)benzene (**4c** and **4t**) was obtained. As reported in an earlier paper,[1] the reaction of *cis*-(*p*-cyanostyryl)cobaloxime (**1c**) with bromine gave *cis*- and *trans*-styryl bromides. The formation of *trans*-styryl bromide was shown to be due to the isomerization of the *cis*-*p*-cyanostyryl bromide formed initially. The non-stereospecificity of the reaction of **1c** in the present study, therefore, is thought due to the isomerization of *cis*-2,4-dinitro-1-(*p*-cyanostyrylthio)benzene (**4c**) to the *trans*-isomer (**4t**) under the reaction conditions.

Table 1. Products and yields of the sulfenylation of styryl-type cobaloxime

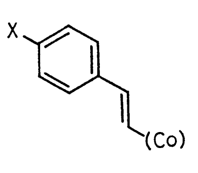
Starting material	Product	Yield %	Starting material	Product	Yield %
1c	**4c, 4t** (44 : 56)	98	**1t**	**4t**	95
2c	**5c**	*ca.* 100	**2t**	**5t**	*ca.* 100
3c	**6c**	*ca.* 100	**3t**	**6t**	*ca.* 100



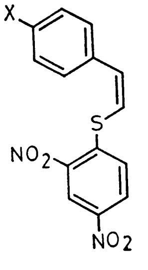
(Co)



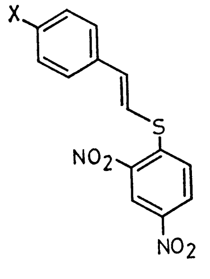
1c, 2c, 3c



1t, 2t, 3t



4c, 5c, 6c

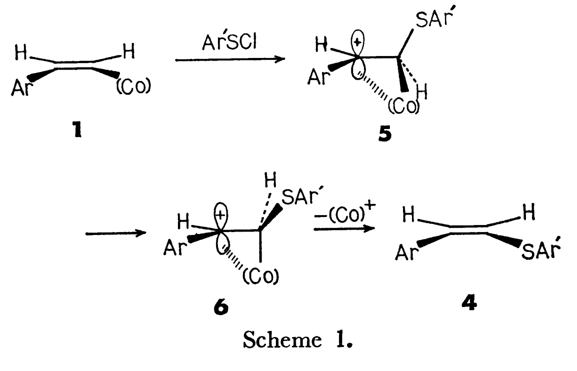


4t, 5t, 6t

(**1c, 1t, 4c, 4t**): $X=CN$ (**2c, 2t, 5c, 5t**): $X=H$
(**3c, 3t, 6c, 6t**): $X=OCH_3$

The basic nature of the present reaction is thought to be the same as that of bromination. The steric consequence of bromination has been discussed in some detail[1] in which the interaction between the benzylic cation and cobalt(III) by p_π-d_π[9] or σ-π conjugation[10] was important. Bond rotation is hindered in the intermediates **5** and **6** in the reaction scheme due to this type of interaction. The mechanistic feature of the present sulfenylation, therefore, can be shown correctly by the scheme shown here. The reaction of **1**, **2**, and **3** with benzenesulfenyl chloride gave (styrylthio)benzenes in the same manner but with less stereospecificity.

In the experiments it was found that styryl-type



Scheme 1.

cobaloximes do not react with hard electrophiles[11] such as isoamyl nitrite and ethyl chloroformate. Soft but weak electrophiles, such as diphenyl disulfide and *N*-(phenylthio)succinimide, again do not react with styryl-type cobaloximes. This property of styryl-type cobaloximes can be attributed to the soft nature and p_π-d_π interaction of cobalt(III). The olefinic carbon of styryl-type cobaloxime, therefore, must acquire a more soft and less nucleophilic property, a property stemming from p_π^*-d_π back-donation from cobalt(III) which diminishes the reactivity of the olefinic carbon towards electrophiles.

In conclusion, soft and strong electrophiles, such as bromine, mercury(II) acetate, and arenesulfenyl chloride, smoothly substitute the cobaloxime group of styryl-type cobaloximes *via* an addition-elimination mechanism as shown in the scheme.

Experimental

Styryl-type cobaloximes (**1**, **2**, and **3**) were prepared by the methods reported[1] and 2,4-dinitrobenzenesulfenyl chloride was prepared by the method of Kharasch and Langford[12] from 2,4-dinitrochlorobenzene. Melting points are not corrected and IR spectra were measured using KBr disks. The NMR spectra were measured in DMSO-d_6 and chemical shifts have been expressed by δ values using sodium 3-(trimethylsilyl)propanoate-d_4 as an internal standard.

Reaction of Cobaloximes with 2,4-Dinitrobenzenesulfenyl Chloride. To a solution of one of the styryl-type cobaloximes (0.25×10^{-3} mol) in dichloromethane (10 ml) was added dropwise 2,4-dinitrobenzenesulfenyl chloride (0.28×10^{-3} mol) dissolved in dichloromethane (2 ml) with magnetic stirring. The reaction mixture was stirred for 1 h after addition of the reagent under nitrogen at ambient temperature (*ca.* 27 °C). The reaction mixture was passed through an alumina column (Merck act. II—III) and the column further eluted by chloroform. Condensation of the combined eluates gave 2,4-dinitro-1-(styrylthio)benzenes (Table 1). Recrystallization of the products from DMF–ethanol gave the pure sulfides. In the case of **1c** the product was a mixture of isomers, which was separated into **4c** and **4t** by chromatography on silica gel eluted by chloroform and recrystallization from DMF–ethanol. **4c**: Mp 149—151 °C. High resolution mass, Found: *m/e* 327.0300. Calcd for $C_{15}H_9N_3O_4S$: *m/e* 327.0313. IR, 2230, 1600, 1340, 920, 900, 850, 830, 745, and 730 cm^{-1}. NMR, 7.18, 7.46 (2H, AB-type, *J*=11 Hz), 7.96 (4H, s), and 8.0—9.1 (3H, dinitrobenzene moiety). **4t**: Mp 219—219.5 °C. Found: C, 55.28; H, 2.72; N, 13.02%. Calcd for $C_{15}H_9N_3O_4S$: C, 55.05; H, 2.77; N, 12.84%. IR, 2225, 1595, 1340, 960, 950, 800, 745, and 730 cm^{-1}. NMR, 7.44, 7.72 ((2H, AB-type, *J*=16 Hz), 7.96 (4H, s), and 8.0—9.1 (3H, dinitrobenzene moiety). **5c**: Mp 104—105 °C. High resolution mass, Found: *m/e* 302.0381. Calcd for $C_{14}H_{10}N_2O_4S$: *m/e* 302.0361. IR, 1595, 1340, 837, 793, 730, and 695 cm^{-1}. NMR, 6.86, 7.36 (2H, AB-type, *J*=11.0 Hz), 7.44—7.88 (5H, m), and 8.0—9.2 (3H, dinitrobenzene moiety). **5t**: Mp 166.5—168 °C. High resolution mass, Found: *m/e* 302.0381. Calcd for $C_{14}H_{10}N_2O_4S$: *m/e* 302.0361. IR, 1590, 1335, 825, 750, 733, and 695 cm^{-1}. NMR, 7.48 (2H, t, *J*=16 Hz), 7.60—7.90 (5H, m), and 8.0—9.1 (3H, dinitrobenzene moiety). **6c**: Mp 160—161 °C. Found: C, 54.85; H, 3.31; N, 8.51%. Calcd for $C_{15}H_{12}N_2O_5S$: C, 54.22; H, 3.64; N, 8.43%. IR, 1594, 1334, 1310, 1260, 830, 770, 745, and 735 cm^{-1}. NMR, 3.82 (3H, s), 6.62, 7.23 (2H, AB-type, *J*=11 Hz), 7.03, 7.62 (4H, AA′BB′-type, *J*=9 Hz), and 7.9—9.0 (3H, dinitrobenzene moiety). **6t**: Mp 203—204 °C. Found: C, 54.33; H, 3.54; N, 8.48%. Calcd for $C_{15}H_{12}N_2O_5S$: C, 54.22; H, 3.64; N, 8.43%. IR, 1598, 1340, 1315, 1255, 830, 800, 750, and 735 cm^{-1}. NMR, 3.87 (3H, s), 7.04, 7.68 (4H, AA′BB′-type, *J*=9.5 Hz), 7.10, 7.30 (2H, AB-type, *J*=16 Hz), and 7.8—9.2 (3H, dinitrobenzene moiety).

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