

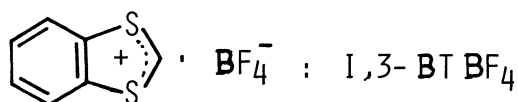
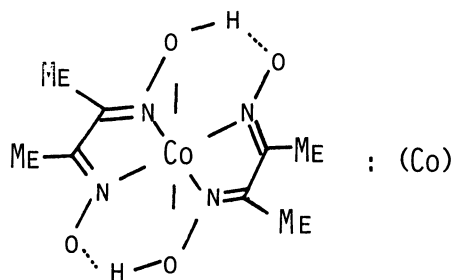
REACTION OF STYRYL-TYPE BIS-DIMETHYLGLYOXIMATO(PYRIDINE)-
COBALT(III), STYRYL COBALOXIMES, WITH
1,3-BENZODITHIOLYL IUM TETRAFLUOROBORATE

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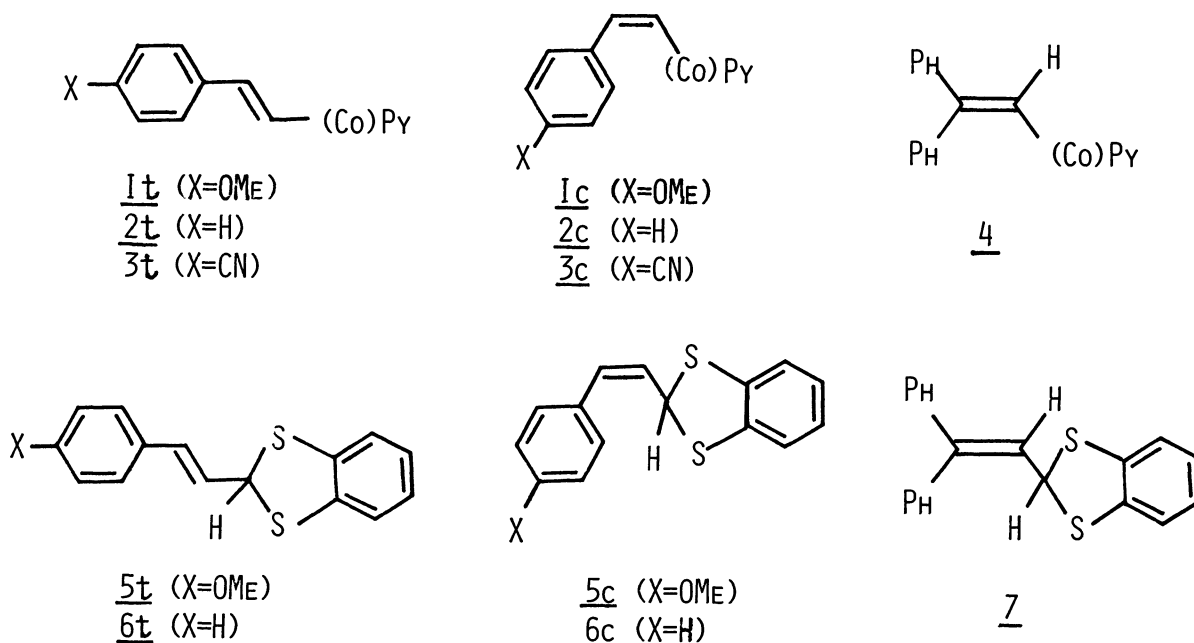
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Styryl-type cobaloximes give the coupling products, 2-styryl-1,3-benzodithioles, by the reaction with 1,3-benzodithiolylium tetrafluoroborate. The trans isomers of styryl cobaloximes are more reactive and more stereospecific than the cis isomers. A mechanism involving a CT-state and electron transfer is proposed.

The carbon-metal bond of vinyl-type complexes of transition metal is cleaved by electrophiles and vinyl-type substitution products are formed with retention of configuration in polar solvents.¹⁻⁴⁾ We have studied the reaction of styryl-type bis-dimethylglyoximato(pyridine)cobalt(III) (a conventional name styryl cobaloxime is used hereafter), with bromine and sulfenyl chlorides and found that the reaction proceeded stereospecifically with retention to give styryl bromide^{4a)} and styrylthiobenzenes⁵⁾ in high yields. In this paper we wish to report the reaction of styryl-type cobaloximes with 1,3-benzodithiolylium tetrafluoroborate (1,3-BTBF₄).⁶⁾ 1,3-BTBF₄ is expected to be a soft electrophile having a wide spread π -orbital and two sulfur atoms and may alter the nature of reaction process.



One of the styryl-type cobaloximes^{4a)} (0.42×10^{-3} mol.) was treated under nitrogen with 1,3-BTBF₄ (0.42×10^{-3} mol.) in dry dichloromethane (3 ml) freed of methanol and the reaction mixture was stirred in the dark at room temperature until the cobaloxime was essentially consumed. Passing of the product mixture through a column of Florisil (ca. 5g) using dichloromethane as eluent gave 2-(styryl)-1,3-benzodithioles as main products and 1,3-benzodithiole (1,3-BT) as a by-product. The length of the reaction time and the yields of the products are listed in the table. The structures of 2-(styryl)-1,3-benzodithioles, 5-7, were deduced from the signal pattern in NMR spectra and elemental analyses, and were confirmed by the hydrolyses catalyzed with chloramine-T and mercuric ion to give cinnamaldehyde and its derivatives.



An electron withdrawing cyano substituent on para-position of styrene moiety hinders the reaction. This fact implies that the electron density at the olefin moiety is important factor in the present reaction. Other features are the less reactivity and stereospecificity of cis-styryl derivatives (1c, 2c). These features must not entirely owing to the large steric interaction between the aryl group and the planar ligands of the cobaloxime since the cobaloxime 4 having one phenyl group in cis-configuration does give the coupling product 7 in reasonable yield. The low stereospecificity with 1c and 2c is probably due to the cis-trans isomerization of the products as seen in the bromination of cis-styryl type cobaloximes.^{4a)} Common by-product in these reactions is 1,3-benzodithiole (1,3-BT),⁷⁾

Table. Reaction of styryl-type cobaloximes with 1,3-BTBF₄

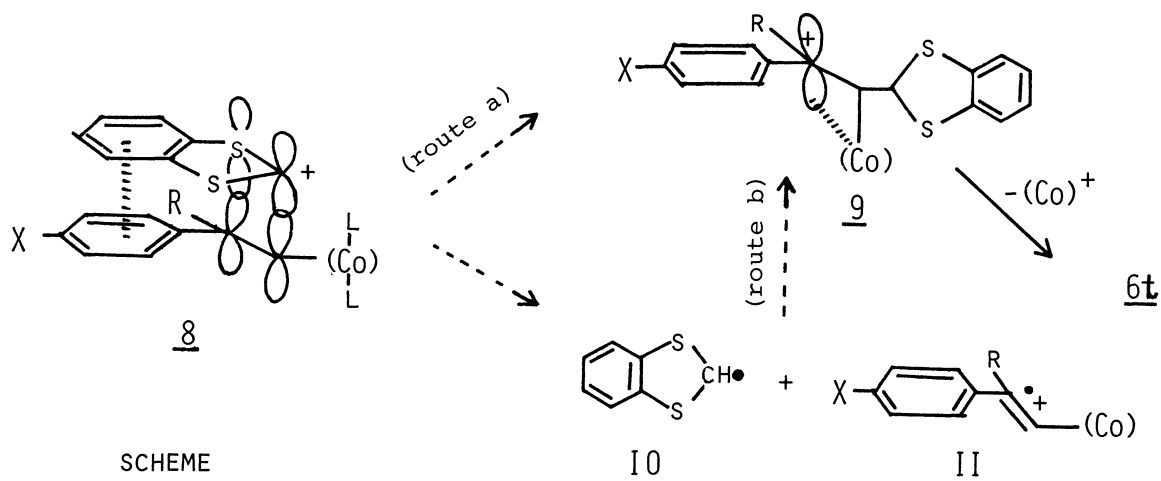
Starting material	Reaction time (h)	Product (yield, %) ^{a)} (mp, °C)	By-product ^{a)} (yield, %)
<u>1t</u>	0.5	<u>5t</u> (96) (103)	-----
<u>2t</u>	2	<u>6t</u> (64) (76)	1,3-BT (8)
<u>3t</u>	14 ^{b)}	Recovered <u>3t</u> in 84%	1,3-BT (6)
<u>1c</u>	2	<u>5c</u> (17) (83) <u>5t</u> (15)	1,3-BT (trace)
<u>2c</u>	20	<u>6c</u> (4) (66) <u>6t</u> (8)	1,3-BT (14)
<u>3c</u>	14 ^{b)}	Recovered <u>3c</u> in 46%	p-cyanostyrene (40)
<u>4</u>	14	<u>7</u> (55) (112)	1,3-BT (trace), 1,1-diphenyl-ethylene (30)

a) Isolated yield after separation by chromatography on Florisil (hexane - carbon tetrachloride)

b) Most of the starting material was left intact.

which must be formed through 1,3-benzodithiolyl radical (10), and styrene derivative. Low material balance in the reactions of 1c and 2c must be due to the loss of p-methoxystyrene and styrene, respectively, by polymerization and evaporation during work up. Thus the formation of 1,3-BT is an evidence for an electron transfer from the cobaloximes to 1,3-BTBF₄. Though the formations of p-cyanostyrene and 1,1-diphenylethylene from 3c and 4, respectively, without 1,3-BT are ambiguous, a radical ion (11) can be expected to give the styrene derivatives.

These features of the reaction of cobaloximes 1-4, are different from those of the bromination of 1-3 in several aspects. The effect of para-substitution on the reactivity is larger in the present reaction than in bromination. The difference in reactivities between cis (1c, 2c) and trans isomers (1t, 2t) is also different in the present reaction and bromination. These discussions prompted us to propose a mechanism shown in the scheme, which is little different from that of bromination.^{4a)} A strong CT-interaction can be envisaged by the soft nature of 1,3-BTBF₄ and the electronic accommodation of the styryl-type cobaloximes. The CT-state (8) may require a rather strict and intimate arrangement of the both partners. In the case of cis-isomers (1c, 2c), a large steric hindrance between



1,3-BTBF₄ and the planar dimethylglyoximate ligands must exist and the reaction becomes sluggish. The CT-state (8) proceeds to give a cation (9) (route a), in which the bond rotation is prohibited by the interaction between the cation center and the cobalt ion.^{4a)} The elimination of cobaloxime cation from 9 gives the product with retention of configuration. Electron transfer in 8 gives radical species 10 and 11, which are the precursors of 1,3-BT and styrene derivatives respectively. The radical coupling between 10 and 11 also gives the cation 9 (route b). The selection of the route a or b as the path to 9 is difficult from the present results.

References and Note

- 1) Hg-complex: a) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968). b) C. P. Casey, G. H. Whitesides, and J. Kurth, *J. Org. Chem.*, **38**, 3406 (1973).
- 2) Zr-complex: D. W. Hart, T. F. Blackburn, and J. Schwartz, *J. Amer. Chem. Soc.*, **97**, 679 (1975).
- 3) Cu-complex: H. Westmijze, H. Kleijn, and P. Vermeer, *Tetrahedron Lett.*, **1977**, 2023.
- 4) Co-complex: a) H. Shinozaki, M. Kubota, O. Yagi, and M. Tada, *Bull. Chem. Soc. Jpn.*, **49**, 2280 (1976). b) D. Dodd, M. D. Johnson, B. S. Meeks, D. M. Titchmarsh, K. N. V. Duong, and A. Gaudemer, *J. C. S. Perkin Trans. II*, **1976**, 1262.
- 5) M. Tada, H. Shinozaki, and K. Miura, under submission.
- 6) a) J. Nakayama, *Synthesis*, **1975**, 38. b) I. Degani and R. Fochi, *ibid*, **1976**, 471.
- 7) Another common by-product is 2-methoxy-1,3-benzodithiole, which was formed in the course of work up, by the reaction of unreacted 1,3-BTBF₄ with methanol contained in commercially available dichloromethane in small amount.

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