Stereospecific Halogenolysis of β-Styrylpyridinecobaloximes. A New General Synthesis of Isomeric β-Halogenostyrenes

By M. D. JOHNSON

(*Department of Chemistry, University College London, Gordon St., London* WC1H OAJ)

and B. S. MEEKS*

(*Department of Chemistry, Moorhead State College, Moorhead, Minnesota* 56560)

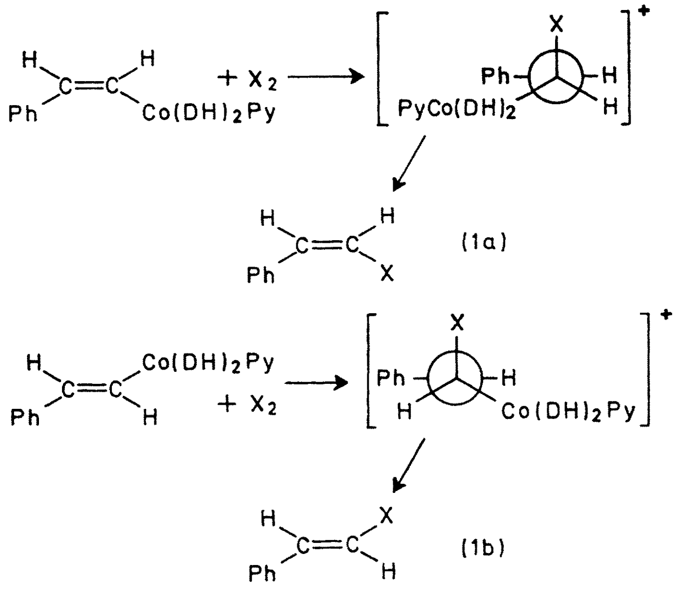
Summary Both *cis*- and *trans*-β-styrylpyridinecobaloximes react by electrophilic substitution with elemental halogens in acetic acid to give the corresponding *cis*- and *trans*-β-halogeno-styrenes in high yields and with complete retention of configuration.

THE *cis*- and *trans*-isomers of β-styrylpyridinecobaloxime can readily be prepared in *ca.*50% yields from inexpensive starting materials.[1] The pure *cis*-isomer is formed, free from both the *trans*-isomer and the α-styryl isomer, by addition of pyridinecobaloxime(I) to phenylacetylene in methanolic solution of rather high alkalinity. The pure *trans*-isomer can be obtained free of the *cis*-isomer by the substitution reaction of pyridinecobaloxime(I) with the commercially available mixture of *cis*- and *trans*-β-bromostyrenes. We now report that these two compounds can be used as starting materials in a simple and completely stereospecific synthesis of the *cis*- and *trans*-isomers of β-chloro-, β-bromo-, and β-iodo-styrenes.

Stereospecific syntheses have not been reported for the *cis*- and *trans*-β-chlorostyrenes, which have been obtained pure by separation of the isomer mixture.[2] β-Iodostyrene has been reported[3] without comment on its isomeric composition. Halogenolysis of β-styrylcobaloximes renders all these compounds available in a pure form. The reaction is not applicable to the preparation of fluorostyrenes.

Dilute solutions of the halogens in acetic acid were added dropwise at 20° to equimolar quantities of the appropriate β-styrylpyridinecobaloximes dissolved in acetic acid. The resulting reaction mixtures were diluted with water and extracted with petroleum. The extract was washed with sodium hydrogen carbonate solution, dried, and examined by n.m.r. (Table). In each of the six cases the product had the same configuration as the starting material and contained no detectable amount of the other isomer.

The results suggest direct electrophilic substitution. A free-radical reaction would not be expected to give perfect stereoselectivity. Likewise, if addition occurred to give the (2-phenyl-1,2-dihalogenoethyl)cobaloxime, this type of compound must necessarily both be formed from all three halogens and undergo elimination of halogenocobaloxime with perfect stereoselectivity. This would not be expected. It seems probable, therefore, that the reaction proceeds generally as shown in the Scheme, with a very rapid carbon–cobalt bond cleavage.



DH = dimethylglyoxime monoanion; Py = pyridine

SCHEME

The preparation of *cis*-β-iodostyrene is typical of these reactions. It occurs with quantitative yield, based upon the *cis*-β-styrylpyridinecobaloxime, even when carried out on a crude material formed by addition of pyridinecobaloxime(I) to phenylacetylene under conditions such that it was contaminated with a substantial amount of the isomeric α-styrylpyridinecobaloxime. The amount of the *cis*-β-styryl isomer in the crude material was assayed by n.m.r. No purification of the crude styrylcobaloxime, other than washing, was required. The quantitative yield of the *cis*-β-iodostyrene clearly indicates the synthetic usefulness of the reaction.

^{1}H *n.m.r. spectra*[a] *for β-halogeno-styrenes. Chemical shifts of the vinylic proton doublets.*

Halogen	Isomer	τ (p.p.m.)	*J*(Hz)
Cl	*cis*	3·49; 3·89	8·5
Cl	*trans*	3·21; 3·53	14·4
Br	*cis*	3·07; 3·72	8·3
Br	*trans*	—[b]; 3·39	14·0
I	*cis*	—[b]; 3·56	8·8
I	*trans*	—[b]; 3·32	15·0

[a] Determined on petroleum extract (Me_4Si as internal standard) using Perkin-Elmer R-10, 60 MHz instrument.

[c] Downfield doublet partially obscured by phenyl proton absorption.

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