The Bromination and the Mercuration of Bis(dimethylglyoximato)-(styryl)pyridinecobalts(III), Styryl-type Cobaloximes

Hiraku SHINOZAKI, Minoru KUBOTA, Osamu YAGI, and Masaru TADA*

Department of Chemistry, School of Science and Engineering, Waseda University, Shinju-ku, Tokyo 160

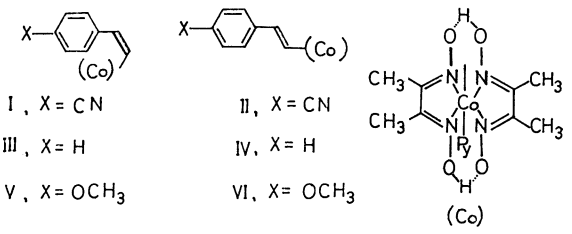
(Received February 20, 1976)

cis and *trans-p*-Cyanostyryl(pyridine)cobaloximes (I and II) and *cis* and *trans-p*-methoxystyryl(pyridine)-cobaloximes (V and VI) were prepared by the reaction of the reduced form of cobaloxime, bis(dimethylglyoximato)-(pyridine)cobalt(I), with *cis* and *trans-p*-cyanostyryl bromides and with *cis* and *trans-p*-methoxystyryl bromides, respectively. The styryl-type cobaloximes thus obtained retained the stereochemistry, *cis* or *trans*, of the starting bromides. The bromination of these styryl-type cobaloximes (I, II, V, and VI) and of the *cis* and *trans*-styryl-(pyridine)cobaloximes (III and IV) in polar or non-polar solvents gave styryl-type bromides with the retention of configuration. The mercuration of these cobaloximes with mercury(II) acetate in DMF gave styryl-type mercurials, again retaining the original configuration.

In recent years much attention has been paid to the stereochemistry of the electrophilic substitution of alkylmetal complexes,[1] especially bis(dimethylglyoximato)-(alkyl)pyridinecobalt(III) (its conventional name, alkyl-(pyridine)cobaloxime, will be used hereafter). Little is known, however, about the stereochemistry of the electrophilic fission of vinyl-type cobalt complexes, though Johnson and Meeks[2] reported the halogenation of styryl(pyridine)cobaloxime in acetic acid and we reported the bromination and the mercuration of 1-octenyl(pyridine)cobaloxime in several solvents,[3] The halogenation of *cis* and *trans*-styryl(pyridine)cobaloxime takes place with the retention of configuration in acetic acid[2] and the bromination of *cis* and *trans*-1-octenyl-(pyridine)cobaloxime takes place with the retention and the inversion of the configuration[3] (Eq. 1).

$$\text{R-CH=CH-(Co)} \xrightarrow{Br_2} \text{R-CH=CH-Br} + \text{Br-(Co)} \quad (1)$$

We examined the steric course of the bromination and the mercuration of *para*-substituted and non-substituted styryl(pyridine)cobaloximes in varying reaction conditions to get a deeper insight into the reaction mechanism, referring to the electronic effect of the substituent on the benzene ring.



I, X = CN II, X = CN

III, X = H IV, X = H

V, X = OCH_3 VI, X = OCH_3

Syntheses of Styryl-type Cobaloximes. *cis* and *trans-p*-Cyanostyryl(pyridine)cobaloxime (I and II) were synthesized by the reaction of *p*-cyanostyryl bromides with the reduced form of pyridinecobaloxime,[4] prepared *in situ* from a dimeric bis(dimethylglyoximato)(pyridine)-cobalt(II), by a reduction using zinc powder in methanol. The similar reactions of *cis* and *trans-p*-methoxystyryl bromides were sluggish and did not give *p*-methoxystyryl(pyridine)cobaloximes (V and VI) in a reasonable yield. *p*-Methoxystyryl(pyridine)cobaloximes (V and VI), therefore, were synthesized by the action of the cobaloxime anion, bis(dimethylglyoximate)(pyridine)cobalt(I), prepared *in situ* from dimethylglyoxime, cobalt(II) chloride, pyridine, sodium hydroxide, and sodium tetrahydroborate in methanol. *cis* and *trans*-Styryl(pyridine)cobaloximes (III and IV)[5] were prepared similarly, by the reaction of *cis* and *trans*-styryl bromides with the cobaloxime anion.

The stereochemistry of the styryl-type cobaloximes is easily assigned from the coupling constants of the olefinic protons in the NMR spectra of these cobaloximes; 10 Hz, 9 Hz, and 9 Hz for I, III, and V, and 15 Hz, 15 Hz, and 14 Hz for II, IV, and VI, respectively. The steric course of the reactions of styryl bromides has been reported to be completely stereospecific with retention of configuration,[5] and the reactions with *p*-cyanostyryl bromides or *p*-methoxystyryl bromides also took the stereospecific course with retention. The rate of the displacement reaction of these bromides with cobaloxime anions is much faster at the *trans*-bromide than at its *cis*-isomer, and we needed the pure *cis para*-substituted styryl bromides for the preparations of *cis* styryl-type cobaloximes. The base treatment of *erythro*-2,3-dibromo-3-(*p*-methoxyphenyl)-propionic acid gave only *trans-p*-methoxystyryl bromide under various conditions. The base treatment of *erythro*-2,3-dibromo-3-(*p*-acetoxyphenyl)propionic acid[6] gave stereoselectively *cis-p*-acetoxystyryl bromide or its *trans*-isomer, depending upon the reaction conditions. The treatment of the dibromide with triethylamine in a non-polar solvent such as benzene gave *cis-p*-acetoxystyryl bromide exclusively. On the other hand, the treatment of the dibromide with sodium acetate in water afforded only *trans-p*-acetoxystyryl bromide. *cis-p*-Acetoxystyryl bromide was converted into *cis-p*-methoxystyryl bromide by hydrolysis of the acetoxy group followed by methylation.

Electrophilic Reaction of Styryl-type Cobaloximes. Bromination of the styryl-type cobaloximes was carried out with an equivalent amount of bromine; the reaction took place smoothly at room temperature and almost instantly in polar solvents to give the corresponding styryl-type bromides in high or quantitative yields. The compositions of the styryl bromides from each reaction are collected in Table 1. The bromination of *p*-cyanostyryl(pyridine)cobaloximes (I and II) and styryl(pyridine)cobaloximes (III and IV) in methanol gave bromides retaining the original configurational most exclusively, though the bromination of

* To whom correspondence should be addressed.

p-methoxystyryl(pyridine)cobaloximes (V and VI) gave 1,1-dibromo-2-methoxy-2-(*p*-methoxyphenyl)ethane, due to the facile methoxybromination of the resulting *p*-methoxystyryl bromides. The bromination of all six cobaloximes in dichloromethane or benzene proceeded with retention. In carbon disulfide, the reaction of *cis*-cobaloximes (I, III, or V) with an equivalent amount of bromine gave products with extensive inversion (I, 45%; III, 12%, V; 20% inversion respectively). These results were proved to be due to the isomerization of the *cis*-bromides to their *trans*-isomers under the reaction conditions from the following experimental findings. The composition of the bromides from *cis*-cobaloximes (I, III, or V) depends upon the amount of bromine used and approaches the limiting values (Fig. 1).

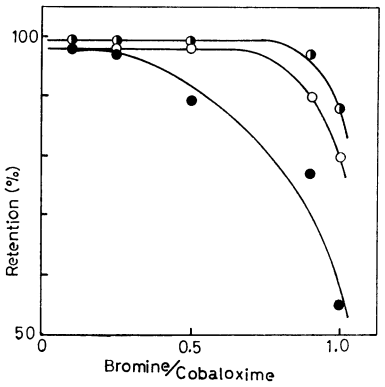


Fig. 1. Stereospecificity in the bromination of cobaloximes with varying amount of bromine.
a) ● (I), ◑ (III), ○ (V).
b) In carbon disulfide at room temperature.

These limiting values were obtained by extrapolation of the curves to an infinite amount of the bromine used, and are collected in Table 1. Brominations of the cobaloximes, therefore, are proved to proceed with retention even in carbon disulfide. This feature is in sharp contrast with the bromination of *cis* and *trans*-1-octenyl(pyridine)cobaloxime, which gives products with a preferential inversion in carbon disulfide.[3] We reexamined the bromination of 1-octenyl(pyridine)-cobaloxime with varying amounts of bromine, but no significant difference from the earlier results was observed. A temperature-effect upon the product composition was found in the case of the bromination of 1-octenyl(pyridine)cobaloxime[3] and we found that the bromination of styryl-type cobaloximes in refluxing carbon disulfide (46 °C) gave the styryl-type bromides with inversion to some extent. The compositions in Table 1 are again the limiting values from the reaction with 0.25 equivalent amount of bromine. These data show that the bromination itself takes place with a complete retention in carbon disulfide even at a higher temperature. Next, we examined the relative reactivities of the *trans*-cobaloximes (II, IV, and VI) and *trans*-1-octenyl(pyridine)cobaloxime to bromine by carrying out a competitive reaction. The relative reactivities thus obtained are 1.0 (II), 2.3 (1-octenyl(pyridine)-cobaloxime), 3.1 (IV), and 4.7 (VI); this sequence of the reactivity is accounted for by the electrophilic nature of the reaction, though a more profound difference in the reactivity, in general, can be expected for a typical electrophilic reaction of *para*-substituted styrenes.[7]

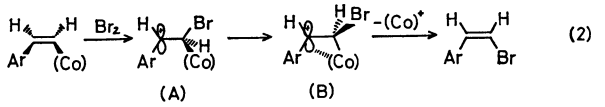
One of the possible explanations of the stereochemical consequence of the bromination is the hindered rotation of the bond between the benzylic carbon and the carbon-bearing cobaloxime moiety in an intermediate (B), which either formed in concert with the attack of bromine or formed stepwise *via* an intermediate (A) (Eq. 2). This inhibition of rotation must be due to the stereoelectronic stabilization of the benzylic cation by either a vertical stabilization,[8] originating from the conjugation between the vacant *p*-orbital and the σ-bond of carbon–cobalt, or a d-π conjugation between the vacant *p*-orbital and a filled d-orbital of the cobalt ion.[9] The rupture of the cobaloxime moiety from the cation (B) is expected to afford styryl-type bromides which retain the original configuration of the starting cobaloximes.

Dodd and Johnson[10] have described briefly, in a review article, the mercuration of the cobaloximes III and IV in acetic acid; they pointed out that inconsistent results were obtained depending on the purity of the solvent. Our mercuration of the cobaloximes (I—VI) with mercury(II) acetate in DMF, followed by the treatment with sodium chloride, gave the styryl-type mercurials. NMR analysis of the resulting mercurials dissolved in DMSO showed that the product retained the original stereochemistry of the cobaloximes. No stereochemical consequence is further altered, regardless of whether the *para*-substituent is electron

Table 1. Isomeric compositions (%) of the styryl-type bromides from bromination of styryl-type cobaloximes

Starting material	I		II		III		IV		V		VI	
Solvent \ Bromide	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
MeOH[a]	92	8	3	97	100	trace	trace	100	c)	c)	c)	c)
C_6H_6[a]	96	4	1	99	100	trace	trace	100	98	2	2	98
CH_2Cl_2[a]	97	3	2	98	100	trace	trace	100	96	4	6	94
CS_2[a]	98	2	3	97	100	trace	6	94	98	2	6	94
CS_2[b]	97	3	trace	100	100	trace	trace	100	98	2	trace	100

a) Reaction temperature: *ca.* 20 °C (room temperature). b) Reaction temperature: 46 °C (reflux). c) 1,1-Dibromo-2-methoxy-2-(*p*-methoxyphenyl)ethane was obtained.



(2)

donating ($-OCH_3$) or electron withdrawing (-CN), and the mercuration must take the same steric course as the bromination.

In conclusion the bromination and the mercuration of *para*-substituted styryl(pyridine)cobaloximes take place with the retention of configuration to give styryl-type bromides and styrylmercury(II) chlorides in high yields; these results can be accounted for by the intervention of the benzylic cation stabilized by neighboring group participation of a cobaloxime moiety.

$$X\text{-}C_6H_4\text{-}CH{=}CH\text{-}(Co) + Hg(OAc)_2 \xrightarrow[DMF]{NaCl} X\text{-}C_6H_4\text{-}CH{=}CH\text{-}HgCl$$

Table 2. Isomeric compositions of the styryl-mercury(II) chlorides from mercuration of the styryl-type cobaloximes in DMF

Starting material	I	II	III	IV	V	VI
Yield(%)	82	49	100	84	95	49
cis(%)	97	4	100	trace	94	3
trans(%)	3	96	trace	100	6	97

Experimental

Styryl-type Bromides. *cis* and *trans*-Styryl bromide,[11,12] *cis* and *trans-p*-cyanostyryl bromides,[13] and *trans-p*-methoxystyryl bromide[14] were prepared by the reported methods. *cis-p*-Methoxystyryl bromide was prepared from *erythro*-2,3-dibromo-3-(*p*-acetoxyphenyl)propionic acid, mp 187—189 °C, which was prepared by the same procedure as that used for the prepartion of *erythro*-2,3-dibromo-3-(phenyl)propionic acid.[6]

The mixture of *erythro*-2,3-dibromo-3-(*p*-acetoxyphenyl)-propionic acid (50 g, 0.137 mol), 35 ml of triethylamine, and 250 ml of benzene was refluxed for 2 h, then the mixture was filtered to remove the triethylamine hydrobromide. The filtrate was washed successively with water, saturated aqueous $NaHCO_3$, and 2M HCl, and was dried over Na_2SO_4. The condensation of the solution gave a mixture of *cis* and *trans-p*-acetoxystyryl bromides (*cis*/*trans*=84/16) as an oil (22 g). The solution of these *p*-acetoxystyryl bromides (22 g) in ethanol (80 ml) and water (20 ml) was mixed with 4 ml of concd HCl and then refluxed for 2 h. Most of the ethanol was evaporated under reduced pressure and the aqueous solution thus obtained was extracted with benzene after the addition of more water. The benzene extract was wased with saturated aqueous $NaHCO_3$ and was dried over Na_2SO_4. Evaporation of benzene from the solution gave a light yellow solid, which was purified by passing through a silica gel column (2.5×25 cm) with hexane–ether (1 : 1) to give *p*-hydroxystyryl bromides (15.7 g). For the purification of *cis-p*-hydroxystyryl bromide, the *p*-hydroxystyryl bromides were esterified with benzoyl chloride–pyridine, and the recrystallization of the benzoates from hexane–carbon tetrachloride gave *cis-p*-benzoyloxystyryl bromide. Mp 93 °C, IR(KBr): 1730 and 700 cm^{-1}. NMR($CDCl_3$): 6.36 (1H, d, J=8 Hz) and 6.98 ppm (δ) (1H, d, J=8 Hz).

Hydrolysis of the *cis-p*-benzoyloxystyryl bromide (8.2 g) with sodium hydroxide (2.7 g) in ethanol–water (6 : 1) gave *cis-p*-hydroxystyryl bromide in quantitative yield. The methylation of the bromide by dimethyl sulfate in dry acetone in the presence of K_2CO_3 gave *cis-p*-methoxystyryl bromide (3.5 g, 71%). Bp 128—134 °C/15—16 mmHg. IR(neat): 1600, 1505, 1250, 1175, 1015, 830, and 705 cm^{-1}. NMR (CCl_4): 3.58 (3H, s), 5.96 (1H, d, J=8 Hz), 6.50 (2H, d, J=9 Hz), 6.62 (1H, d, J=8 Hz), 7.26 ppm (δ) (2H, d, J=9 Hz).

Syntheses of Styryl-type Cobaloximes. *cis* and *trans*-Styryl(pyridine)cobaloximes (III and IV) were prepared by the reaction of *cis* and *trans*-styryl bromides with the cobaloxime anion, as reported earlier.[5]

a) *cis* and *trans-p*-Cyanostyryl(pyridine)cobaloximes (I and II). To a mixture of *cis-p*-cyanostyryl bromide (2.1 g, 10 mmol) and dimeric pyridinecobaloxime, $(Co(dmgH)_2py)_2$,[4] (7.3 g, 10 mmol) in 80 ml of methanol was added under nitrogen 2.0 g of zinc powder; the mixture was stirred for 18 h at room temperature. The reaction mixture was filtered and the filtrate was condensed. The residue was dissolved in 70 ml of chloroform, and the chloroform extract was washed with water and dried over Na_2SO_4. The chloroform solution was condensed under reduced pressure and the condensate was passed through a Florisil column (2.7× 18 cm) with chloroform–ethylacetate (1 : 1) to remove impurities. Evaporation of the solvent from the eluate gave essentially pure *cis-p*-cyanostyryl(pyridine)cobaloxime (I) in the yield of 48%. Recrystallization of I from acetonitrile–benzene gave pure cobaloxime (I).

The same procedure starting with *trans-p*-cyanostyryl bromide gave *trans-p*-cyanostyryl(pyridine)cobaloxime (II) in the yield of 66%.

cis-Cobaloxime (I), mp 208—210 °C (decomp). Found: C, 53.15; H, 4.98; N, 16.92%. Calcd for $C_{22}H_{25}N_6O_4Co$: C, 53.23; H, 5.08; N, 16.93%. IR (KBr): 2230, 1600, 1560, 1440, 700, 550, 520 cm^{-1}. NMR ($CDCl_3$): 1.92 (12H, s), 5.99 (1H, d, J=10 Hz), 6.39 (1H, d, J=10 Hz), 7.06—7.86 (7H, m), 8.42—8.60 ppm (δ) (2H, m).

trans-Cobaloxime (II), mp 216—224 °C (decomp). Found: C, 53.24; H, 5.07; N, 17.10%. Calcd for $C_{22}H_{25}N_6O_4Co$: C, 53.23; H, 5.08; N, 16.93%. IR (KBr): 2230, 1605, 1565, 1450, 975, 700, 550, 520 cm^{-1}. NMR ($CDCl_3$): 2.14 (12H, s), 6.30 (1H, d, J=15 Hz), 7.40—8.00 (8H, m), 8.60—8.85 ppm (δ) (2H, m).

b) *cis* and *trans*-Methoxystyryl(pyridine)cobaloximes (V) and (VI). *cis*-Cobaloxime (V) was synthesized by the reaction of *cis-p*-methoxystyryl bromide (1.0 g, 4.7 mmol) with the cobaloxime anion prepared *in situ* from $CoCl_2\cdot 6H_2O$ (0.95 g, 4 mmol), dimethylglyoxime (0.93 g, 8 mmol), 8 ml of 10 M-sodium hydroxide, pyridine (0.5 g), and sodium tetrahydroborate (200 mg) under nitrogen in methanol (40 ml) at 0 °C for 1 h and at room temperature for 1.5 h. The reaction mixture was extracted with benzene (50 ml× 2) after the addition of water (100 ml). The condensation of the extract after drying over Na_2SO_4 gave the residue containing *cis*-cobaloxime (V). This residue was passed through a Florisil column (2.5×20 cm) with dichloromethane and dichloromethane–ethyl acetate (2 : 1). Evaporation of the solvent from the latter fraction gave *cis*-cobaloxime (V). Recrystallization of the cobaloxime (V) from acetonitrile gave pure V in the yield of 39%.

The same procedure starting with *trans-p*-methoxystyryl bromide gave *trans-p*-methoxystyryl(pyridine)cobaloxime (VI) in the yield of 45% after recrystallization.

cis-Cobaloxime (V), mp 198—204 °C (decomp). Found: C, 52.63; H, 5.44; N, 14.00%. Calcd for $C_{22}H_{28}N_5O_5Co$:

C, 52.70; H, 5.63; N, 13.97%. IR (KBr): 1610, 1595, 1510, 1450, 1240, 850, 770, 705, 530 cm^{-1}. NMR ($CDCl_3$): 1.84 (12H, s), 3.60 (3H, s), 5.24 (1H, d, J=9 Hz), 6.10 (1H, d, J=9 Hz), 6.46 (2H, d, J=9 Hz), 6.66 (2H, d, J=9 Hz), 6.86—8.22 ppm (δ) (5H, pyridine).

trans-Cobaloxime (VI), mp 215—218 °C (decomp). Found: C, 52.49; H, 5.51; N, 14.26%. Calcd for $C_{22}H_{28}N_5O_5Co$: C, 52.70; H, 5.63; N, 13.97%. IR (KBr): 1600, 1500, 1440, 1230, 950, 830, 750, 510 cm^{-1}. NMR ($CDCl_3$): 2.00 (12H, s), 3.58 (3H, s), 5.86 (1H, d, J=14 Hz), 6.46 (2H, d, J=8 Hz), 6.59 (1H, d, J=14 Hz), 6.88 (2H, d, J=8 Hz), 7.00—8.44 ppm (δ) (5H, pyridine).

Reaction of Cobaloximes (I—VI) with Bromine. The solution of one of the cobaloximes (I—VI) (0.2 mmol) in one of the solvents (15 ml) depicted in Table 1 was treated with an equivalent amount of bromine in 1 ml of the same solvent, and the mixture was stirred for 30 min at room temperature under nitrogen. When carbon disulfide was used as a solvent, the volume of the solution was increased to 40 ml and the reaction at 46 °C was carried out by boiling the reaction mixture. The reactions with smaller equivalents of bromine were carried out in the same manner to get the limiting values listed in Table 1. After the reaction the mixture was filtered, the filtrate was condensed, and the residue was dissolved in hexane–ether (1 : 1). Passing of the solution through an alumina column (Merck II-III, 0.8×5 cm) with hexane–ether (1 : 1) gave the corresponding styryl-type bromides. The product composition was determined by a GLC analysis (2.1 m, 5%-PEG-Succinate on Chromosorb P, N_2). Identification of the bromides as *cis* and *trans*-styryl-type bromides was made by the comparison of GLC and NMR spectra of the products with those of authentic samples.

Competitive Reaction. A solution containing equal amounts (0.2 mmol) of cobaloximes II, IV, and VI was treated with 0.02 mmol of bromine and stirred for 20 min at room temperature under nitrogen. The reaction mixture was worked up as described above and the relative amounts of styryl-type bromides were determined by GLC analyses. For this purpose the relative sensitivity of the bromides in GLC analyses was determined by analyzing a mixture of the bromides with known composition. The mixture of 0.2 mmol of *trans*-styryl(pyridine)cobaloxime and *trans*-1-octenyl(pyridine)cobaloxime was subjected to the same treatment.

Mercuration of Cobaloximes (I—VI). The solution of one of the cobaloximes (I—VI, 0.2 mmol) in DMF (10 ml) was treated with 1.2 equivalents of mercuric acetate and the mixture was stirred for 30 min at room temperature. The mixture was further stirred for 10 min after addition of 2 ml of saturated aqueous solution of sodium chloride and was extracted with chloroform after further addition of water (10 ml). The extract was washed with water and dried over Na_2SO_4. Evaporation of chloroform and DMF at reduced pressure gave a styryl-type mercurial. The crude product thus obtained was passed through a silica gel column (1.0× 10 cm) with chloroform and evaporation of the solvent gave styryl-type mercury(II) chloride with retention in the yield listed in Table 2. The product composition was determined by the relative intensities of the NMR signals of the olefinic hydrogens of the product. The structure of the mercurials was confirmed by transforming these organomercury(II) chlorides into the corresponding styryl-type bromides with bromine in pyridine. *cis*-Cyanostyrylmercury(II) chloride, mp 184—185 °C. IR (KBr): 2220, 1405, 850, 540 cm^{-1}. NMR (DMSO): 6.53 (1H, d, J=12 Hz), 7.56 (1H, d, J=12 Hz), 7.95 ppm (δ) (4H, s).

trans-Cyanostyrylmercury(II) chloride, mp 232—233 °C. IR (KBr): 2230, 1500, 1170, 970, 850, 780, 550 cm^{-1}. NMR (DMSO): 6.92 (2H, s), 7.63, 7.85 ppm (δ) (4H, AB-type, J=8 Hz).

cis-Styrylmercury(II) chloride, mp 106.5—107 °C. IR (KBr): 1580, 1560, 1480, 1440, 1325, 770, 680 cm^{-1}. NMR (DMSO-d_6): 6.30 (1H, d, J=12 Hz), 7.30—7.90 ppm (δ) (6H, m).

trans-Styrylmercury(II) chloride, mp 210—211 °C. IR (KBr): 1590, 1560, 1490, 1440, 965, 720 cm^{-1}. NMR (DMSO-d_6): 6.60, 6.85 (2H, AB-type, J=18 Hz), 7.05—7.50 ppm (δ) (5H, m).

cis-Methoxystyrylmercury(II) chloride, mp 97—98 °C. IR (KBr): 1610, 1510, 1260, 1170, 830 cm^{-1}. NMR (DMSO-d_6): 3.80 (3H, s), 6.15 (1H, d, J=11 Hz), 7.20 (2H, d, J=9 Hz), 7.43 (1H, d, J=11 Hz), 7.65 ppm (δ) (2H, d, J=9 Hz).

trans-Methoxymercury(II) chloride, mp 220—222 °C. IR (KBr): 1600, 1510, 1250, 1170, 1020, 960, 830, 770 cm^{-1}. NMR (DMSO-d_6): 3.80 (3H, s), 6.50, 6.85 (2H, AB-type, J=19 Hz), 6.96 (2H, d, J=9 Hz), 7.40 ppm (δ) (2H, d, J=9 Hz).

References

1) H. Shinozaki, H. Ogawa, and M. Tada, *Bull. Chem. Soc. Jpn.*, **49**, 775 (1976) and references cited therein.

2) M. D. Johnson and B. S. Meeks, *Chem. Commun.*, **1970**, 1027.

3) M. Tada, M. Kubota, and H. Shinozaki, *Bull. Chem. Soc. Jpn.*, **49**, 1097 (1976).

4) "Inorganic Syntheses," ed. by W. L. Jolly, McGraw Hill, Vol. XI, N. Y. (1968), p. 61.

5) M. D. Johnson and B. S. Meeks, *J. Chem. Soc., B*, **1971**, 185.

6) M. Reimer, *J. Am. Chem. Soc.*, **64**, 2510 (1942).

7) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1483 (1969); J. E. Dubais and A. Schwarz, *Tetrahedron Lett.*, **1964**, 2169.

8) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971).

9) G. E. Coates, M. L. H. Green, and K. Wada, "Organometallic Compounds," Methuen, Vol. 2, London (1968), p. 215.

10) D. Dodd and M. D. Johnson, *J. Organomet. Chem.*, **52**, 77 (1973).

11) S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 2645 (1953).

12) L. J. Dolby, C. Wilkins, and T. F. Frey, *J. Org. Chem.*, **31**, 1110 (1953).

13) W. Davies, B. M. Holmes, and J. F. Kefford, *J. Chem. Soc.*, **1939**, 357.

14) E. R. Trumbull, R. T. Finn, K. M. Ibne-Rasa, and C. K. Sauers, *J. Org. Chem.*, **27**, 2339 (1962).