propylamine (1.1 mol). The solution was cooled to 0 °C, and 0.54 mL of *n*-butyllithium (2.05 M in hexane) was added dropwise. After 15 min the solution was cooled to −78 °C and a 1 M solution of the silyl ester (1.0 mmol) in THF was added dropwise. After the reaction solution was stirred for 30 min, 1.1 mL of a 1 M solution of $BrCH_2CHO$ in THF was added at once. After being stirred for 5 min, the reaction was quenched with 0.13 mL (2.3 mmol) of acetic acid and the resultant suspension was warmed to 0 °C. A saturated solution of aqueous $NaHCO_3$ (3 mL) was added, and the two-phase system was stirred vigorously for 5 h. The ice bath was allowed to warm to ambient temperature. The reaction mixture was diluted with brine (5 mL) and was extracted with 3 × 10 mL of Et_2O. The organic phase was dried over Na_2SO_4. Upon removal of solvent some silylated material was present. Complete conversion to the hydroxy lactone was accomplished by dissolving the crude product in 3 mL of methylene chloride and adding ca. 0.5 mL of a 1 M solution of tetra-*n*-butylammonium fluoride in THF. The reaction was stirred at ambient temperature until TLC analysis showed disappearance of high R_f material (15–20 min). The solution was diluted with 5 mL of Et_2O and washed with 1 × 3 mL of water and 1 × 3 mL of brine. The aqueous layers were combined and reextracted with 3 mL of ether. The ethereal layer was dried over Na_2SO_4. Purification was effected by filtration through a small amount of silica gel with ethyl ether.

Entry 1: IR (film) 3460, 2970, 1770, 1100 cm^{-1}; 60-MHz NMR ($CDCl_3$) δ 1.23 (s, 6 H), 3.92–4.50 (m, 4 H); high-resolution mass spectrum for $C_6H_{10}O_3$ requires *m/e* 130.063 00, found 130.063 35.

Entry 2: IR (film) 3460, 2960, 1775, 1170 cm^{-1}; NMR ($CDCl_3$) δ 0.93 (br, 3 H), 1.12–2.00 (m, 9 H), 2.30–2.62 (m, 1 H), 3.90 (br s, 1 H), 4.00–4.67 (m, 3 H); high-resolution mass spectrum for $C_8H_{13}O_3$ ($M^+ - 1$) requires *m/e* 157.086 47, found 157.086 88.

Entry 3: IR (film) 3460, 2970, 1780, 1255, 840 cm^{-1}; NMR ($CDCl_3$) 2.3–2.7 (m, 3 H), 3.63 (br s, 1 H), 4.0–4.6 (m, 3 H), 4.92–5.32 (m, 2 H), 5.50–6.20 (m, 1 H); high-resolution mass spectrum for $C_7H_{10}O_3$ requires *m/e* 142.063 00, found 142.063 52.

Entry 4: IR (film) 3490, 1770, 1165, 750, 690 cm^{-1}; NMR ($CDCl_3$) δ 3.20 (br s, 1 H), 3.80–4.30 (m, 4 H), 6.70–7.30 (m, 5 H).

Entry 5: IR (film) 3460, 1780, 1590, 1490, 1230, 1100, 905, 725 cm^{-1}; NMR ($CDCl_3$) δ 3.62 (br s, 1 H), 4.0–5.0 (m, 4 H), 6.80–7.50 (m, 5 H).

Entry 6: IR (film) 3440, 2980, 1770, 1020, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.58 (s, 3 H), 3.81 (br s, 1 H)8 4.10–4.40 (m, 3 H), 7.10–7.80 (m, 5 H); high-resolution mass spectrum for $C_{11}H_{12}O_3Se$ requires *m/e* 271.995 12, found *m/e* 271.995 62.

Entry 8. The isomers were separated by flash chromatography using 3:1 ether:hexane. Trans isomer: IR (film) 3460, 2940, 1770, 1180, 1025 cm^{-1}; 300-MHz NMR ($CDCl_3$) δ 1.62 (br s, 6 H), 1.70 (br s, 3 H), 1.80–2.30 (m, 8 H), 2.48 (m, 1 H), 3.09 (br s, 1 H), 4.00–4.60 (m, 3 H), 5.12 (br t, 2 H); high-resolution mass spectrum for $C_{15}H_{24}O_3$ requires *m/e* 252.172 55, found 252.173 09. Cis isomer: IR (film) 3460, 2930, 1765, 1450, 1275, 1140, 1040, 975 cm^{-1}; 300-MHz NMR ($CDCl_3$) δ 1.63 (br s, 9 H), 2.00 (m, 8 H), 2.40 (m, 1 H), 2.78 (br s, 1 H), 4.23 (d, 2 H), 4.47 (m, 1 H), 5.13 (br t, 2 H); high-resolution mass spectrum for $C_{15}H_{24}O_3$ requires *m/e* 252.172 55, found 252.173 67.

Dendrolasin (1). Compound **3a** (0.29 mmol) was dissolved in 1 mL of CH_2Cl_2 and cooled to 0 °C. Triethylamine (0.6 mmol) was added followed by addition of neat methanesulfonyl chloride (0.3 mmol). The reaction was stirred and allowed to warm slowly to room temperature over 5 h. The reaction was diluted with 5 mL of Et_2O and was washed once with 2 mL saturated $NaHCO_3$ (aqueous) and then once with brine. The organic layer was dried over Na_2SO_4. The crude butenolide was sufficiently pure to be taken to the next step. The butenolide (0.3 mmol) was dissolved in 3.5 mL of dry THF and was added to a flask containing a nitrogen atmosphere. After the solution was cooled to −20 °C, 0.40 mL of Dibal (1 M in hexane) was added dropwise. TLC analysis after 1 h revealed the disappearance of starting material. The reaction was quenched with 0.03 mL of acetic acid and was warmed to room temperature. After washing with 2 mL of saturated $NaHCO_3$ (aqueous) and 2 mL of brine, the organic phase was dried over Na_2SO_4. Removal of solvent left a viscous yellow oil, which contained small amounts of furan by NMR but a large OH stretch in the IR. This material was dissolved in 3 mL of CH_2Cl_2 and treated with a catalytic amount of pTSA·H_2O for 3 h until TLC analysis showed one major spot (R_f 0.85 in 1:1 Et_2O:hexane. The solution was diluted with hexane and filtered through 3 of silica gel with hexane. Removal of the solvent left 20.5 mg of a colorless oil, which was shown to be dendrolasin. This was obtained in 32% yield from **3a**. This was shown to be dendrolasin by comparison with literature data.[11]

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Registry No. **1**, 23262-34-2; **3a** (isomer 1), 87727-61-5; **3a** (isomer 2), 87727-62-6; **6**, 24120-56-7; $BrCH_2CHO$, 17157-48-1; $(CH_3)_2CHCO_2SiMe_3$, 16883-61-7; $BuCH_2CO_2SiMe_3$, 14246-15-2; $H_2C{=}CHCH_2CH_2CO_2SiMe_3$, 23523-56-0; $C_6H_5OCH_2CO_2SiMe_3$, 21273-08-5; $C_6H_5SCH_2CO_2SiMe_3$, 55724-31-7; $C_6H_5Se(CH_3)CHCO_2SiMe_3$, 87683-16-7; $Br_2CHCO_2SiMe_3$, 37977-60-9; $H(CH_2C(CH_3){=}CHCH_2)_2CH_2CH_2CO_2SiMe_3$, 87683-17-8; α,α-dimethyl-β-hydroxybutyrolactone, 87683-09-8; α-butyl-β-hydroxybutyrolactone, 87683-10-1; α-allyl-β-hydroxybutyrolactone, 87683-11-2; α-phenoxy-β-hydroxybutyrolactone, 87683-12-3; α-(phenylthio)-β-hydroxybutyrolactone, 87683-13-4; α-(phenylseleno)-α-methyl-β-hydroxybutyrolactone, 87683-14-5; α,α-dibromo-β-hydroxybutyrolactone, 87683-15-6; α-(4,8-dimethyl-3,7-nonadienyl)-β-hydroxybutyrolactone, 87727-60-4.

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Formation of *trans*-Stilbenes from 1,1-Dichloro-2,2-diarylethanes: A New Cobaloxime-Mediated Carbenoid Rearrangement

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Organocobalt compounds with a rigid planar ligand system have attracted considerable attention as model systems for vitamin B_{12}.[1] Among these, bis(dimethylglyoximato)cobalt(I) ("cobaloxime", **1**) is perhaps one of the best known. Interest in alkylcobaloximes has been steadily growing due to their use as models for biological systems and as intermediates in interesting synthetic transformations.[2] Investigations have concentrated mainly on alkylcobaloximes obtained by displacement of organic halides by the "supernucleophilic" Co(I) species. The ready homolysis of the Co–C bond in these compounds has been synthetically exploited, and a number of radical displacements,[3] couplings,[4] and rearrangements[5] have been reported. In comparison to the wealth of information regarding the interaction of bis(dimethylglyoximato)cobalt (I) with alkyl halides, very little is known about the re-

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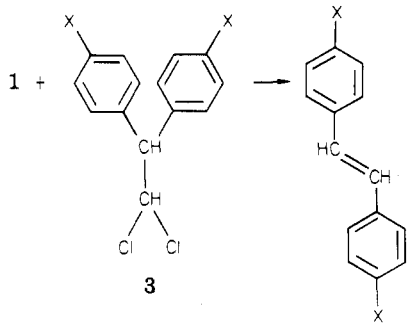
Scheme I[a]



3 4

[a] X = H, a; CH_3, b; CH_2CH_3, c; OCH_3, d; Br, e; Cl, f.

Table I. Formation of Stilbenes 4 from 1,1-Dichloro-2,2-diarylethanes 3

compd	X	cobalt complex	% yield	mp, °C	lit. mp, °C
3a	H	DMG[a]	79	124	124[b]
3b	CH_3	DMG	63	181	179-180[c]
3c	CH_2CH_3	DMG	53	132	134[d]
3d	OCH_3	DMG	57	211	211[e]
3e	Br	DMG	49	212	210[f]
3f	Cl	DMG	49	176	175-176[g]
3f	Cl	Salen[a]	38	176	175-176[g]
3f	Cl	B_{12s}	63	176	175-176[g]

[a] DMG = bis(dimethylglyoximato), Salen = bis(*N,N'*-disalicylalethylenediamine). [b] "Beilsteins Handbuch der Organischen Chemie"; Springer Verlag: Berlin, 1943, Vol. Vol. 5(II), p 537. [c] *Ibid.* 1943, Vol. 5(II), p 558. [d] *Ibid.* 1922, Vol. 5, p 651. [e] *Ibid.*, 1923, Vol. 6, p 1023. [f] *Ibid.*, 1922, Vol. 5, p 635. [g] See ref 21.

action of this and related compounds with geminal dihalides.

While investigating the interaction of chlorinated pesticides with vitamin B_{12}, we had previously come across an interesting rearrangement of 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD) in the presence of vitamin B_{12s} to form *trans*-4,4'-dichlorostilbene.[6,7] We now demonstrate the generality of this novel rearrangement for cobaloxime and related systems with a variety of 1,1-dichloro-2,2-diarylethanes.

The 1,1-dichloro-2,2-diarylethanes **3** were prepared by reaction of the corresponding arenes with dichloroacetaldehyde diethyl acetal in the presence of concentrated sulfuric acid.[8] Addition of **3** to a solution of bis(dimethylglyoximato)cobalt(I) (**1**), generated in situ by reduction under nitrogen with excess sodium borohydride of the corresponding Co(II) species, gave *trans*-4,4'-disubstituted phenylstilbenes **4** in moderate to good yields (Scheme I, Table I). The reaction is not restricted to cobalamines and cobaloximes. When bis(*N,N'*-disalicylalethylenediamine)cobalt(I) (**2**, Co^ISalen) was employed instead of cobaloxime **1**, stilbene **4** was obtained, though in a lower yield. A rigid, planar ligand system seems essential, however, for the cobalt complexes that undergo this reaction. When the dichlorodiarylethane **3f** (DDD) was added to a solution of $CoCl_2$ and sodium borohydride, no *trans*-4,4'-dichlorostilbene (**4f**) was formed; under these conditions DDD was simply dechlorinated to R_2CHCH_2Cl and R_2CHCH_3. Thus, the rearrangement described depends strongly on the nature of the ligands around the cobalt atom. Among the cobalt complexes tested, vitamin B_{12} proved to be the best reagent to effect this rearrangement. A much smaller ratio of cobalt complex/substrate was used in the case of B_{12} than either cobalt glyoximate or Co^I Salen, and a higher yield of rearranged stilbene **4f** was obtained.

Inspection of Table I shows that the yields of stilbenes formed do not vary significantly with the different aryl substituents X. This rules out a carbenium ion rearrangement as a possible pathway for the reaction. We are then left with two possibilities which are compatible with the above observation: a radical or a carbenoid rearrangement.

The suggestion of a radical rearrangement was first put forward by Stotter[9] to account for the formation of *trans*-4,4'-dichlorostilbene in the reaction of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) with chromous chloride. More recent reports of radical rearrangements of alkylcobaloximes[5] might support this first alternative. However, our own observations that the reaction of 1-chloro-2,2-bis(*p*-chlorophenyl)ethane (DDM) with vitamin B_{12s} does not lead to the formation of any stilbene[6] but to a stable alkylcobalamine[7] clearly invalidates the intermediacy of R_2CHCH_2Cl as proposed in the original scheme. Furthermore, radicals $R_2CH-\dot{C}HCl$ and $R_2CH-\dot{C}H_2$, generated by interaction of DDD and DDM, respectively, with vitamin B_{12r}, do not rearrange.[10] We can thus rule out a radical rearrangement as a possible pathway for this reaction.

The second alternative, a carbenoid rearrangement, finds support in the observation that carbenes are generated by the interaction of vitamin B_{12s} with multihalogenated hydrocarbons.[11] Cobaloxime carbenes have indeed been isolated and characterized.[12] In order to provide evidence for a carbenoid pathway, we submitted DDD to conditions known to lead to carbenoid species. The reaction of geminal dihalides with copper and catalytic amounts of iodine has been described as a variation of the Simmons–Smith procedure for the addition of carbenes to double bonds.[13] A metal carbenoid is postulated for this reaction. Although we did not expect the reaction with copper to follow an identical pathway as our reaction with cobalt(I) dimethylglyoximate, we reasoned that the formation of *trans*-4,4'-dichlorostilbene from DDD under carbene-generating conditions would give strong support to the hypothesis of a rearrangement via a transition-metal carbenoid. After a 65-h reflux in toluene, the product of the reaction of DDD with Cu/I_2 consisted of a mixture of 4,4'-dichlorostilbene (8%) and unreacted substrate, as shown by GLC analysis. This result reinforces the carbenoid hypothesis. We then sought further support to this hypothesis in the investigations of Castro and Kray[14] on the reactions of chromous chloride with polyhalomethanes. The authors suggested for these reactions the intermediacy of "a carbenoid entity of attenuated reactivity". The reaction of DDT with chromous chloride gave a mixture of products, of which *trans*-4,4'-dichlorostilbene comprised about 50%.[15] The reaction was found to proceed via

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DDD, which was the precursor of the stilbene. This result indicates a difference of behavior of DDT and DDD under the same conditions: DDT is only dechlorinated to DDD while DDD rearranges to the dichlorostilbene.

In order to compare our system with the above reaction, which, according to Castro and Kray[14] should proceed via carbenoid intermediates, we reacted DDT with vitamin B_{12s}. A mixture of products was obtained, of which the 4,4′-dichlorostilbene comprised about 45%. The chlorinated stilbene, RCH=C(Cl)R, which should arise from a direct rearrangement of DDT, in a manner analogous to the DDD rearrangement, was not formed. Our results thus parallel the reaction of DDT with chromous chloride in the sense that, here again, DDD behaved differently in the presence of B_{12s}. DDT, contrary to DDD, does not rearrange but simply dechlorinates to DDD.

In conclusion, the present paper reports an interesting rearrangement of geminal dichloroethanes **3** in the presence of vitamin B_{12s} analogues. Although the reaction is not restricted to cobalt complexes, the smoothness and ease of the conversion, as compared to those of other methods, are noteworthy. Thus, rearrangements take place at room temperature in 5–15 min with reasonable yields. Much longer reaction times and more drastic conditions are required to effect the same transformation with other metal salts, and the yields are much lower. The reported reaction is also interesting from a mechanistic point of view. Our results point to a cobalt carbenoid complex as the rearranging species in the formation of stilbenes from dichloroethanes **3**. Many questions regarding the exact nature of this species remain to be answered. Nevertheless, our results represent a contribution to a better understanding of metal carbenoid chemistry, in particular to the little explored field of alkylcobaloxime rearrangements.

Experimental Section

^{1}H NMR spectra were determined on a Varian Model T-60 with $(CH_3)_4Si$ as an internal reference. Infrared spectra were measured with a Perkin-Elmer 720 apparatus. Gas chromatographic analyses were obtained with a CG 370 chromatograph. Melting points were taken with a Koffler hot-stage apparatus and are not corrected.

1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD), 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene were purchased from Aldrich Chemical Co., and vitamin B_{12} was purchased from Sigma Chemical Co. The following 1,1-dichloro-2,2-diarylethanes **3** were prepared by reaction of the corresponding arenes with dichloroacetaldehyde diethyl acetal[16] in the presence of sulfuric acid;[8] 1,1-dichloro-2,2-diphenylethane, mp 76 °C (lit.[17] mp 74 °C); 1,1-dichloro-2,2-bis(*p*-methylphenyl)ethane, mp 79 °C, (lit.[17] mp 80 °C); 1,1-dichloro-2,2-bis(*p*-ethylphenyl)ethane, mp 55 °C (lit.[17] mp 56–57 °C); 1,1-dichloro-2,2-bis(*p*-methoxyphenyl)ethane, mp 116 °C (lit.[18] mp 115–116 °C); 1,1-dichloro-2,2-bis(*p*-bromophenyl)ethane, mp 135 °C (lit.[19] mp 133 °C).

Preparation of Stilbenes 4. General Procedure. Sodium borohydride (0.46 g, 12 mmol) was added under nitrogen to a suspension of bis(dimethylglyoximato)cobalt(II)[20] (0.65 g, 1.8 mmol) in methanol–water (3:1, 5 mL). To the resulting dark blue solution was then added, after the gaseous evolution had subsided (2–3 min), a solution of a dichlorodiarylethane (**3**, ca. 1.2 mmol) in methanol (ca. 20 mL) previously flushed with nitrogen. The stilbene **4** began to crystallize out of the reaction mixture after 5 min. The product was filtered after 40 min and recrystallized from ethanol or acetic acid. All stilbenes **4** thus obtained were characterized by their IR and NMR spectra, identical with the spectra of authentic samples. Specific melting points and yields are given in Table I.

Reaction of DDD with B_{12s}. In a similar procedure vitamin B_{12} (0.1 g, 0.074 mmol) and sodium borohydride (0.46 g, 12 mmol) reacted with DDD (0.4 g, 1.2 mmol) to give *trans*-4,4′-dichlorostilbene: 0.196 g (63%); recrystallized from acetic acid; mp 176 °C (lit.[21] mp 175–176 °C); IR (KBr) 3050, 1590, 1490, 1090, 970, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.0 (2 H, s), 7.4 (8 H, m).

Reaction of DDD with Co^{I}Salen. Bis(*N*,*N*′-disalicylalethylenediamine)cobalt(II)[22] (0.65 g, 1.8 mmol) and sodium borohydride (0.46 g, 12 mmol) reacted with DDD (0.4 g, 1.2 mmol) to give *trans*-4,4′-dichlorostilbene (0.12 g, 38%), characterized as above.

Reaction of DDT with Vitamin B_{12s}. A solution of DDT (0.1 g, 2.6 mmol) in methanol (60 mL) was added under nitrogen to a solution of vitamin B_{12s}, generated by treatment of B_{12} (0.1 g, 0.074 mmol) with sodium borohydride (0.1 g, 2.6 mmol) in water (6 mL). After 1 h of reaction, the solution was rotary evaporated, the residue extracted with chloroform (30 mL), and the organic layer analyzed by gas chromatography (column OV-17, column temperature 190 °C). Comparison with authentic samples revealed DDD (18%), *trans*-4,4′-dichlorostilbene (44%), and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (20%) as major components of the product mixture.

Reaction of DDD with Copper. A suspension of DDD (1.28 g, 4 mmol), powdered copper (0.63 g, 10 mmol), and iodine (0.254 g, 1 mmol) in toluene (15 mL) was refluxed for 65 h. The suspension was then filtered and the filtrate analyzed by GLC (column OV-17, temperature 200 °C); only DDD and *trans*-4,4′-dichlorostilbene, in a 92:8 ratio, were detected in the mixture.

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Registry No. 1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethane, 72-54-8; 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, 50-29-3; dichloroacetaldehyde diethyl acetal, 619-33-0; 1,1-dichloro-2,2-diphenylethane, 2387-16-8; 1,1-dichloro-2,2-bis(*p*-methylphenyl)ethane, 26204-07-9; 1,1-dichloro-2,2-bis(*p*-ethylphenyl)ethane, 72-56-0; 1,1-dichloro-2,2-bis(*p*-methoxyphenyl)ethane, 7388-31-0; 1,1-dichloro-2,2-bis(*p*-bromophenyl)ethane, 5216-53-5; benzene, 71-43-2; methylbenzene, 108-88-3; ethylbenzene, 100-41-4; methoxybenzene, 100-66-3; bromobenzene, 108-86-1; sodium borohydride, 16940-66-2; bis(dimethylglyoximato)cobalt(II), 36451-49-7; vitamin B_{12s}, 18534-66-2; bis(*N*,*N*′-disalicylalethylenediamine)cobalt(I), 26220-77-9; copper, 7440-50-8.

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Mechanism of Bromination of 1,5-Diacetoxynaphthalene

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Bromojuglone derivatives have proven to be extremely useful in controlling the regiochemistry of Diels–Alder reactions, particularly in synthetic approaches toward a variety of anthracyclines.[2] Until recently, the reported

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