mol) of **1** (prepared by vacuum sublimation of the hydrate) and 5 ml of 2-bromoethanol was stirred for 45 min at room temperature and then for 15 min at 50°. The clear viscous solution, which showed no carbonyl absorption in the infrared region, was treated with 2.1 ml (0.015 mol) of triethylamine. The temperature rose to *ca.* 60° and a solid was deposited. After 30 min the mixture was added with stirring to 100 ml of 2.5 *N* NaOH and 50 ml of ethanol. The insoluble material was collected and amounted to 5.26 g (99%) of **2**. After recrystallization from ethanol it shrank from 300°, and darkened but did not melt at 350°; no infrared absorption in the OH or C=O stretching regions; nmr signal ($CDCl_3$) at δ 4.27 (sharp singlet).

Anal. Calcd for $C_{12}H_4Cl_{10}O_2$: C, 26.95; H, 0.75. Found: C, 27.22; H, 0.75.

Method B.—A mixture of 10.16 g (0.02 mol) of **1** hydrate and 25 ml of 2-chloroethanol was stirred for 24 hr at room temperature. The solid slowly dissolved during this time. The mixture was cooled in ice and treated with 8.5 ml (0.06 mol) of triethylamine. There was a vigorous exothermic reaction and a solid was deposited. After stirring for 2 hr at room temperature the mixture was added to alkali as in method A. The insoluble product amounted to 9.97 g (93%) of **2**. This material was suitable for dechlorination.

1,3,5,7,8,9,10,11,12,12-Decachlorohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecan-4-one, Cyclic Ethylene Ketal (3).—A 450-mg (0.871-mmol) sample of the parent ketone[6] was mixed with 0.2 ml of 2-bromoethanol. The ketone dissolved in a few minutes to give a viscous solution which showed no carbonyl absorption in the infrared region. After 30 min the reaction mixture was added to 9 ml of 2.5 *N* NaOH and 1.5 ml of ethanol to precipitate 280 mg (57%) of **3**, mp 180–184° (lit.[6] mp 186–188°; mixture melting point undepressed).

2,3,5,6-Tetrachloropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-4-one, Cyclic Ethylene Ketal (4).—From 1.0 g (3.36 mmol) of the ketone[7] and 1.5 ml of 2-bromoethanol, under the conditions used in the preparation of **3**, was obtained 0.82 g (72%) of the ketal **4**, mp 216–220° (lit.[7] mp 219–221°; mixture melting point undepressed).

Pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decan-5-one, Cyclic Ethylene Ketal (5).—To a solution of 55 g (0.103 mol) of **2** in 850 ml of dry tetrahydrofuran, contained in a 5-l. flask with a very efficient condenser, were added 193 ml (2.06 mol) of dry *t*-butyl alcohol and 28.6 g (4.12 g-atoms) of lithium wire, cut into small pieces. The reaction mixture was kept under nitrogen. A very vigorous reaction began after a few minutes and was moderated by cooling as necessary. When it subsided somewhat, heat was supplied to maintain the reflux for a further 1 hr. The reaction mixture was poured onto ice and the product was extracted into 1:1 benzene–ether. The extracts were washed with water and evaporated to leave a dark oil. Glpc[8] showed this to consist of the product (60%) with a major impurity (20%) having a longer retention time and several minor faster moving components. The crude mixture was taken up in 300 ml of acetone, heated to reflux, and treated portionwise with 60 g of finely powdered potassium permanganate. A strong permanganate color persisted in the solution after refluxing for 30 min.[9] The solution was filtered and the filtrate was heated with sufficient methanol to discharge the permanganate color. Filtration and evaporation gave a colorless oil which was partitioned between benzene–ether and dilute Na_2CO_3. The organic phase was washed with water and evaporated to leave 7.0 g of a light yellow oil, 96% pure by glpc, which was distilled at 0.06 mm from a bath at 135° (substantial viscous residue) to give 5.4 g (28%) of **5**, largely crystalline at room temperature and showing no impurities by glpc. This was recrystallized from methanol at −30° and sublimed (65°, 18 mm) to give the pure ketal: mp 32.5–34°; very strong infrared absorption at 9.02 μ (COC);[10] nmr signals (CCl_4) at δ 1.37 (2 H partly resolved triplet, cage CH_2), 2.42, 2.61, and (2.89 2 H, 4 H, and 2 H, respectively, broad singlets, methine CH), and 3.73 (4 H singlet, OCH_2CH_2O).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.50; H, 7.32.

Pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decan-5-one (6).—A 5.85-g sample of **5** (not distilled, 96% by glpc) was refluxed for 6 hr with 60 ml each of benzene and 3 *N* HCl. The aqueous phase was withdrawn and replaced with fresh acid and the mixture was refluxed for a further 4 hr. The benzene layer was separated, washed with water, and evaporated to a partially crystalline residue. This was distilled (sausage flask) at 22 mm with a bath temperature of 165°. The largely crystalline distillate was warmed with 7 ml of pentane and cooled to −30° to yield 1.86 g (15% from **2**) of **6**, mp 125–126°. Recrystallization from pentane raised the melting point to 127–128° (lit. mp 123° [2] and 120–122° [11]): infrared absorption, complex band centered at 5.75 μ (C=O); nmr signals (CCl_4) at δ 1.42 (2 H partly resolved triplet, CH_2), and at 2.58, 2.76, and 3.33 (2 H, 4 H, and 2 H, respectively, broad singlets, methine CH).

Wolff–Kishner reduction of **6** under conditions employed for an isomeric ketone[12] gave pentacyclo[5.30.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane, mp 126–127° (sealed capillary, uncorrected, lit.[12] mp 125–127°). Ketalization with 2,2-dimethoxypropane and methanolic HCl gave the oily dimethyl ketal. The nmr spectra of both the hydrocarbon[12] and the dimethyl ketal[2] were identical with those reported in the literature.

Registry No.—**2**, 15650-61-0; **5**, 15745-98-9; **6**, 15745-99-0.

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(9) In some cases, part of the permanganate formed a cake at the bottom of the flask and did not react. If this occurred, more permanganate was added to complete oxidation of the unsaturated components.

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The Stereochemistry of the Addition of Cobalt Hydrocarbonyl to 1,2-Diphenylcyclobutene-1

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Since the discovery[1] that hydrogen tetracarbonylcobaltate(−I), $HCo(CO)_4$ (commonly called cobalt hydrocarbonyl), is the active form of the catalyst in the oxo reaction, many studies have been reported in which this compound has been used in the stoichiometric hydroformylation of olefins. However, despite the theoretical and commercial importance of the reaction, neither the kinetics nor the stereochemistry of the stoichiometric reaction has been completely established. In one of the few stereochemical studies[2] of the catalytic high pressure oxo reaction, 3,4-di-O-acetyl-D-xylal was shown to yield a product corresponding to *cis* addition of $HCo(CO)_4$. In a related reaction, cyclohexene oxide

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(1) M. Orchin, L. Kirch, and I. Goldfarb, *J. Amer. Chem. Soc.*, **78**, 5450 (1956).

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has been shown[3] to react with $HCo(CO)_4$ to give, after methanolysis of an acylcobalt intermediate, a *trans*-hydroxy ester. A more detailed study[4] of the same reaction showed that one of the major products was a hydroformylated dimer with all-*trans* stereochemistry.

Part of the difficulty of establishing the stereochemistry is the fact that the reaction of $HCo(CO)_4$ with olefins leads to extensive isomerization as well as to mixed products.[5]

During the past few years, we have been investigating substrates which may minimize some of the difficulties commonly encountered in attempts to establish the stereochemistry of the $HCo(CO)_4$ olefin addition. 1,2-Diphenylcyclobutene-1 appeared to be a particularly useful substrate because phenyl-conjugated olefins react with $HCo(CO)_4$ to give hydrogenated products[6,7] and the two possible stereoisomeric 1,2-diphenylcyclobutanes are known.[8]

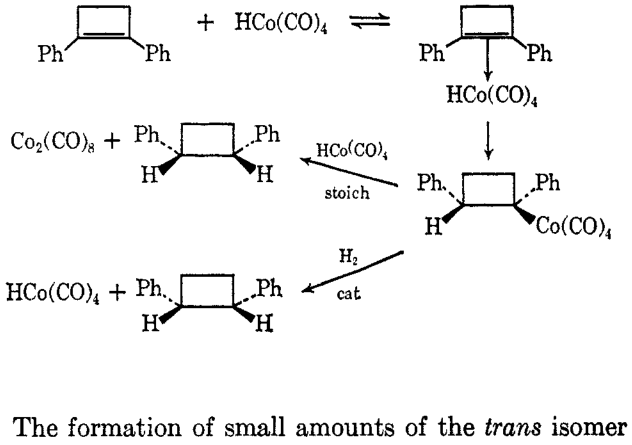
The reaction of 1,2-diphenylcyclobutene-1 with excess cobalt hydrocarbonyl in hexane at room temperature under 1 atm of carbon monoxide gave about 30% conversion into 1,2-diphenylcyclobutanes consisting of less than 4% *trans*- and about 96% *cis*-1,2-diphenylcyclobutane.

1,2-Diphenylcyclobutene was also hydrogenated by subjecting it to high pressure oxo conditions. Nmr and vpc analyses showed complete conversion into the cyclobutanes consisting of 10% *trans* and 90% *cis* isomer.

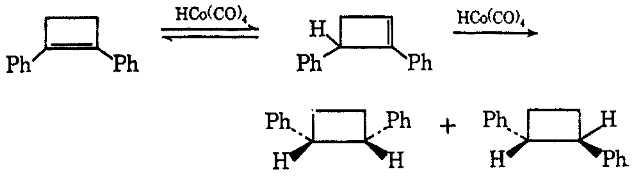
An authentic sample of *cis*-1,2-diphenylcyclobutane, subjected to the same reaction conditions under which hydrogenation of 1,2-diphenylcyclobutene occurred, showed no isomerization to the *trans* isomer either under room or high pressure conditions.

The predominant formation of the *cis* isomer is most easily explained by the reaction sequence involving an alkylcobalt tetracarbonyl[9] as an intermediate (Chart I).

CHART I



The formation of small amounts of the *trans* isomer may be explained by the isomerization of 1,2-diphenylcyclobutene by cobalt hydrocarbonyl[10] and subsequent *cis* addition of cobalt hydrocarbonyl to the isomeric diphenylcyclobutene. The *cis* addition to the isomerized diphenylcyclobutene can occur from either the top or the bottom, leading to *cis* and *trans* products.



Experimental Section

Melting points were taken on a Fisher-Johns block and are uncorrected. Nmr spectra were taken on a Varian A-60 spectrometer and ir spectra on a Perkin-Elmer Infracord 337. Vpc data were obtained on an F & M 700 gas chromatograph (10% Apiezon L on firebrick column, 5 ft × 0.25 in, 230°, flow rate 98 cc/min, 40 psi, chart paper speed 1.1 cm/min).

1,2-Diphenylcyclobutene-1 and authentic samples of *cis*- and *trans*-1,2-diphenylcyclobutane were prepared by known methods.[8]

Stoichiometric Reaction of Cobalt Hydrocarbonyl with 1,2-Diphenylcyclobutene-1.—An excess (4.65 mmol) of a 0.39 *M* hexane solution of cobalt hydrocarbonyl was added in three portions over a period of 3 days to 0.30 g (1.45 mmol) of 1,2-diphenylcyclobutene in 15 ml of hexane. The reaction was run in a serum-stoppered flask under an atmosphere of CO. After 3 days, the reaction was quenched with 0.1 *N* NaOH solution, and then the aqueous layer was syringed off and 3 ml of dimethylformamide was added to destroy the dicobalt octacarbonyl. The mixture was stirred overnight, washed with water three times, and the hexane layer was dried over magnesium sulfate and then evaporated to dryness. The nmr[8] of a $DCCl_3$ solution of the residue showed clearly that the two major components of the reaction mixture were *cis*-1,2-diphenylcyclobutane and unchanged 1,2-diphenylcyclobutene-1 and that about a 30% conversion into 1,2-diphenylcyclobutane had occurred. Vpc analysis showed three components, eluted at 7, 9, and 16 cm relative to chloroform, which was used as the solvent. Authentic samples of *cis*- and *trans*-1,2-diphenylcyclobutane and 1,2-diphenylcyclobutene-1 were eluted at 7, 9, and 16 cm, respectively. By using a 20% Apiezon L column at 230° (other conditions the same), the resolution between the *cis*- and *trans*-diphenylcyclobutanes was increased and peak integration showed less than 4% *trans*.

Catalytic Hydrogenation of 1,2-Diphenylcyclobutene.—Solutions of 0.54 g (2.59 mmol) 1,2-diphenylcyclobutene-1 in 30 ml of hexane and 0.34 g (0.99 mmol) of dicobalt octacarbonyl in 35 ml of hexane were introduced into a 300-ml Magnadrive autoclave. The autoclave was pressured with 1500 psi each CO and H_2 at room temperature, heated to 110° for 2 hr (3750 psi) and cooled gradually to room temperature. The reaction mixture was worked up in the same manner as the room temperature reaction. The nmr analysis showed complete reaction and vpc analysis indicated about 10% *trans*- and the rest *cis*-1,2-diphenylcyclobutane. For further identification, a small amount of pure *cis* isomer was crystallized from ethanol (mp 38–39° (lit.[8] mp 38–39°)). The same distribution of isomers was obtained with methanol as a solvent.

Attempted Isomerization of *cis*-1,2-Diphenylcyclobutane.—*cis*-1,2-Diphenylcyclobutane was subjected to conditions identical with the room temperature and autoclave reactions and no *trans*-1,2-diphenylcyclobutane could be detected by vpc analysis in either case.

Registry No.—1,2-Diphenylcyclobutene-1, 3306-02-3.

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