that the -CCl=CH- group in **3** has the *trans* configuration.

The formation of only the *trans*-chloro ether **3** from the *trans*-cyclopropane **4** is perhaps more surprising than its formation from **1**, since the proposed intermediate mesomeric ion **5** is asymmetric and could lead to either **3** or to **6** by solvolysis. Some pertinent arguments for the related preferential formation of a single *trans* olefin from *trans*-1,1-dichloro-2-ethoxy-3-methylcyclopropane have been discussed by Skattebøl.[5] We would like to suggest that the ring-opening process is accompanied by solvent attack concerted with ionization, so that the transition state for the process more closely resembles the product **3** than the ion **5**. It is apparent from steric considerations that such an intermediate leading to *trans* **3** would be sterically more favorable than one with the two bulky groups *cis*, leading to **6**.

The preferential loss of chlorine *cis* to hydrogen that occurs with dichlorocyclopropanes derived from *cis* olefins such as *cis*-octene-4 and *cis*-cyclododecene, is not general for cyclopropanes derived from small-ring olefins, such as cyclohexene. It is well known[11] that steric requirements prevent formation of smaller ring *trans* olefins, and requires formation of the *cis* olefin (analogous to eq 3). The rate of elimination of hydrogen chloride from the 1,1-dichlorocyclopropane derived from cyclohexene was studied by Cristol and coworkers[11] in acetic acid at 124.6°; the observed rate constant was 4.5×10^{-7} sec^{-1}.

Experimental Section

cis-**1,1-Dichloro-2,3-dipropylcyclopropane** (**1**) was prepared from octene-4[12] (96% *cis* and 4% *trans*), sodium methoxide[13] (from a fresh bottle), and ethyl trichloroacetate by a procedure essentially identical with that described for the reaction with cyclododecene.[8] The chromatographed product was distilled to give an 89% yield of **1**: bp 77–80° (9 mm); $n^{25}{}_D$ 1.4568. The product was shown by glpc (silicon oil, DC-710, 20% on Chromosorb W) to be **1** contaminated by ~4% of **4**.

Anal. Calcd for $C_9H_{16}Cl_2$: C, 55.39; H, 8.27. Found: C, 55.39; H, 8.43.

trans-**1,1-Dichloro-2,3-dipropylcyclopropane** (**4**) was prepared as described for **1**. The cyclopropane was obtained pure in 82% yield, bp 131–136° (86 mm), $n^{25}{}_D$ 1.4520.

Anal. Calcd for $C_9H_{16}Cl_2$: C, 55.39; H, 8.27; Cl, 36.34. Found: C, 55.54; H, 8.35; Cl, 36.08.

trans-**5-Chloro-6-ethoxy-4-nonene** (**3**). **A. From 4.**—A mixture of **4** (7.81 g, 0.04 mol), absolute ethanol (150 ml), and silver nitrate (7.70 g, 0.045 mol) was heated at the reflux temperature for 48 hr. The cooled mixture was filtered and alcohol was removed (rotatory evaporator). The residue was extracted with petroleum ether (350 ml, bp 55–67°) and washed with two 50-ml portions of water, and the resulting solution was dried ($MgSO_4$) and concentrated. The residue (7.35 g) was chromatographed on alumina (150 g) using petroleum ether as eluent. The first fraction (6.25 g) was recovered **4** (80% recovery). The second compound eluted, and the only product detected, was *trans*-5-chloro-6-ethoxy-4-nonene (**3**, 0.97 g, 12% yield, $n^{25}{}_D$ 1.4420). The ether **3** showed the following spectral data: ir, $\nu_{C=C}$ (1625 cm^{-1}), ν_{C-O-C} (1117 and 1092 cm^{-1}); nmr (20% in CCl_4), C═**CH** (triplet, τ 4.40, J = 7 cps, wt 1), $\mathbf{H_2}$C—O—C**H** (complex, τ 6.28–7.08, wt 3), C═C—$\mathbf{CH_2}$ (quartet, τ 7.81, J = 7 cps, wt 2), and CH_2 and $\mathbf{CH_3}$ (complex, τ 8.27–9.18, wt 15).

Anal. Calcd for $C_{11}H_{21}OCl$: C, 64.53; H, 10.34. Found: C, 64.84; H, 10.04.

B. From 1.—The reaction of **1** (7.81 g) with ethanolic silver nitrate was carried out as described for **4**. There was obtained recovered starting material (1.16 g, $n^{25}{}_D$ 1.4471) and *trans*-5-chloro-6-ethoxy-4-nonene (5.27 g, 64% yield, $n^{25}{}_D$ 1.4421). A small third fraction (0.82 g) was obtained which was principally **3**; the small impurity was not characterized. The nonene **3** was identical (ir and nmr spectroscopy and glpc, silicon oil, DC-710, 20% on Chromosorb W) with the product obtained in A, above.

Kinetic Experiments.—The cyclopropane **4** (1.9513 g, 0.0100 mol) was diluted to the mark in a 50-ml volumetric flask with purified ethanol.[14] Approximately 0.0015 mol (0.2548 g) of silver nitrate was placed quantitatively in each of a number of 50-ml, round-bottom flasks wrapped with tin foil. Three pieces of clean boiling chips and 5 ml of stock cyclopropane solution were added to each flask which were fitted with condensers and drying tubes wrapped with aluminum foil. The flasks were placed in an oil bath maintained at 80.8 ± 0.2°. The flasks were removed successively at intervals from 12 to 525 hr and the contents were cooled quickly with an ice bath. In each case, the mixture was transferred quantitatively to a 250-ml volumetric flask and diluted to the mark with 0.1 *N* potassium nitrate solution containing 0.05% of gelatin. Aliquots of these solutions were pipetted and titrated with 0.1000 *N* standard potassium chloride solution using an amperometric method.[15]

The resulting rate constant was $k_{trans} = 5.33 \times 10^{-7}$ sec^{-1}.

By a similar procedure the rate of reaction of **1** was found to be $k_{cis} = 1.29 \times 10^{-5}$ sec^{-1}. The ratio of k_{cis}/k_{trans} was 24.2.

trans-**6-Ethoxynonene-4** (**9**).—The reduction of **3** (0.641 g, 0.003 mol) was carried out essentially as described for a similar reduction of 2-chloro-2-cyclotridecen-1-ol.[8] The product, collected at 57–70° at 32 mm (80% yield), contained no starting material as determined by glpc (silicon oil, DC 710, 20% on Chromosorb W, $^3/_4$ in. × 80 in. column at 100°) and was nearly pure **9**. A sample collected from the glpc described above showed the following properties: ir, $\nu_{C=C}$ (1662 cm^{-1}), ν_{C-O-C} (1115, 1090 cm^{-1}), and $\nu_{CH=CH\ (trans)}$ (975 cm^{-1}). The nmr spectrum (20% in CCl_4) showed C═**CH** (multiplet, τ 4.22–5.00, wt 2), $\mathbf{H_2O}$—O—**CH** (multiplet, τ 6.27–7.08, wt 3), C═C—$\mathbf{CH_2}$ (quartet, τ 7.97 J = 7 cps, wt 2), and $\mathbf{CH_2}$ and $\mathbf{CH_3}$ (complex, τ 8.28–9.27, wt 15).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.38; H, 12.97.

Registry No.—1, 17288-67-4; **3,** 17322-88-2; **4,** 17288-68-5; **9,** 17288-69-6.

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Oligomerization Catalysts. III. Cyclocodimerization of Conjugated Dienes with Acetylenic Hydrocarbons Catalyzed by Iron(0) Complexes. Synthesis of 1,2-Diphenyl-1,4-cyclohexadiene

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In the first two communications of this series[1,2] we described bis(cyclooctatetraene)iron (Fe(COT)$_2$), a new π complex of zerovalent iron, and the activity of this catalyst, which promotes both the oligomerization of butadiene to 1,3,6,10-*n*-dodecatetraene and to 1,5-cyclooctadiene and the codimerization of butadiene with ethylene to *cis*-1,4-hexadiene.

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TABLE I

CYCLOTRIMERIZATION OF 2-BUTYNE AND OF TOLANE AND CYCLOCODIMERIZATION OF 2-BUTYNE–BUTADIENE AND TOLANE–BUTADIENE

		Catalytic system^a		Reacn conditions^c					
Acetylenic compd	Conjugated diene	Iron compd	Organometallic compd	Solvent^b	Temp, °C	Time, hr	Main, product^d	Conversion,^{e}	Selectivity,^{f}
2-Butyne		$Fe(COT)_2$			18	24	HMB	15–20	99–100
2-Butyne		$FeCl_3$	i-C_3H_7MgCl	DEE	18	24	HMB	15–20	90
Tolane		$Fe(COT)_2$		TL	60	15	HPB	15–20	95–100
2-Butyne	Butadiene	$Fe(COT)_2$			18	48	DMC	55–60	89–90
2-Butyne	Butadiene	$FeCl_3$	i-C_3H_7MgCl	DEE	75	48	DMC	60	80
2-Butyne	Butadiene	FeA_3	n-C_4H_9Li	HP	80	1	DMC	8	Not determined
Tolane	Butadiene	FeA_3	$Al(C_2H_5)_3$	TL	20	48	DPC	70	80–90
Tolane	Butadiene	$FeCl_3$	i-C_3H_7MgCl	DEE	20	48	DPC	80	90

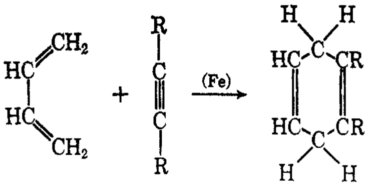
[a] The two-component catalysts were prepared at −40° in the presence of the monomers; FeA_3 = iron tris(acetylacetonate). The organometallic compound/iron compound molar ratio = 5. [b] Abbreviations are as follows: DEE = diethyl ether; HP = n-heptane; TL = toluene. [c] All runs were performed in a glass vessel under an argon atmosphere. [d] Abbreviations are as follows: HMB = hexamethylbenzene; HPB = hexaphenylbenzene; DMC = 1,2-dimethyl-1,4-cyclohexadiene; DPC = 1,2-diphenyl-1,4-cyclohexadiene. [e] Mole % of acetylenic compound reacted/moles of acetylenic compound charged. [f] Mole % of main product/moles of acetylenic compound reacted.

Our studies have now been extended to acetylenic hydrocarbons, which were found to cyclotrimerize and to cyclocodimerize with conjugated dienes by the action of $Fe(COT)_2$. 2-Butyne and diphenylacetylene (tolane) were cyclotrimerized to hexamethylbenzene and to hexaphenylbenzene, respectively. Both acetylenic compounds were cyclocodimerized with 1,3-butadiene to 1,2-disubstituted 1,4-cyclohexadienes. In this note we also report the data found by comparing the catalytic behavior of $Fe(COT)_2$ and of systems obtained by reaction of iron compounds with organometallic compounds.

As known, acetylene and mono (alkyl or aryl) substituted acetylenes yield linear polymers[3] as well as cyclic oligomers[4] in the presence of different catalytic systems. 1,2-Disubstituted acetylenes show a poor tendency to polymerization, but are easily cyclotrimerized to aromatic compounds in the presence of several catalytic agents.[5–7]

The above cyclotrimerizations were obtained by using, as catalysts, $Fe(COT)_2$ or various two-component systems prepared from Fe(III) salts and organometallic compounds (Table I). $Fe(COT)_2$ yields hexaphenylbenzene from tolane when the reaction is carried out at about 50° or at higher temperatures. By operating at lower temperature, a crystalline complex is obtained, the structure of which is still under investigation.

The cyclocooligomerization of acetylenic compounds with conjugated dienes is far less known. The thermal uncatalyzed reaction (Diels–Alder addition) is known only for strongly activated acetylenes as dienophiles or for very active conjugated dienes,[8] like in the case of the formation of norbornadiene from cyclopentadiene and acetylene.[9] The catalytic cycloaddition of 1,2-disubstituted acetylenic hydrocarbons with 2 mol of butadiene yielding 1,4,7-cyclodecatriene derivatives was obtained by Wilke and Heimbach[10] using nickel complexes. Moreover, small amounts of 1,2-divinyl-4-cyclohexene were obtained by Reed[11] from the nickel-catalyzed addition of 2 mol of butadiene to acetylene. By employing the above iron complexes[12] (Table I), we achieved the 1:1 cycloaddition of 1,3-butadiene with 1,2-disubstituted acetylene hydrocarbons to yield 1,2-disubstituted 1,4-cyclohexadienes (eq 1) where (Fe) indicates a catalytic complex containing zerovalent iron, and R indicates either methyl or phenyl.



(1)

Equation 1, which does not occur in the absence of iron catalysts, at least at room temperature, can be formally considered a catalytic Diels–Alder cycloaddition.

1,2-Dimethyl-1,4-cyclohexadiene was identified by comparison with the compound prepared by partial reduction of o-xylene according to Hückel.[13] 1,2-Diphenyl-1,4-cyclohexadiene was characterized by ir, nmr, uv, and mass spectroscopy. The properties of this new compound are described in the Experimental Section.

The cyclocodimerization products were obtained with high selectivities (80–90%) depending on the experimental conditions. We generally used a slight excess of butadiene; thus the by-products mainly consisted of the butadiene oligomers previously described.[1,2] As shown in Table I, the catalytic behavior of the two-component catalysts (except for a slightly higher selectivity of $Fe(COT)_2$) is very similar to that of the latter complex, independently of the organometallic component used to prepare the catalyst.

The analogous behavior of the different catalyst systems used suggests that also the product of the

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(12) With analogous cobalt catalysts only small amounts of the same products were obtained.

(13) W. Hückel and V. Worfell, *Chem. Ber.*, **88**, 338 (1955).

reactions between Fe(III) salts and organometallic compounds in the presence of unsaturated hydrocarbons contains zerovalent iron, which acts as the catalytically active component, to which the unsaturated hydrocarbons are coordinated. However, it cannot be excluded that the metal may undergo a formal oxidation in a transition state, especially in the case of the formation of those linear oligomers, in which hydrogen shift is involved.

In the case of $Fe(COT)_2$ one can reasonably assume that both cyclooctatetraene rings are displaced from their coordination sites by the unsaturated hydrocarbons to be oligomerized with formation of analogous π-type bonds with the metal. We actually observed in the nmr spectrum the progressive formation of free cyclooctatetraene when $Fe(COT)_2$ was dissolved in liquefied butadiene.

As previously indicated, $Fe(COT)_2$, simultaneously and in the same reaction conditions,[2] catalyzes oligomerizations involving hydrogen shift (linear trimerization of butadiene and linear codimerization butadiene–ethylene) as well as cycloadditions (dimerization of butadiene, trimerization of 1,2-disubstituted acetylenes, and codimerizations butadiene–1,2-disubstituted acetylenes), in which hydrogen shift is unnecessary. Hence, it is likely that the reaction of unsaturated hydrocarbons with $Fe(COT)_2$ yields several iron complexes, which are in equilibrium among themselves and which essentially differ in the number of the coordinated double bonds and in their geometric disposition around the metal atom.

Experimental Section

Cyclooligomerization of 2-Butyne Using $Fe(COT)_2$.—In a typical example, a 20-ml glass vial, in which the air had been removed by dry argon, was cooled to −10°, charged with 57 mg of recrystallized $Fe(COT)_2$ and 3 ml of 2-butyne, sealed, and maintained first for 15 hr at −10 to 0° and then 24 hr at room temperature. During this time a large amount of white crystals precipitates from the brown solution. The reaction mixture was dissolved in 20 ml of diethyl ether; the solution was washed with diluted hydrochloric acid and with water and dried ($MgSO_4$). Solvent and excess 2-butyne were distilled and the dry residue was recrystallized from ethanol. A 0.4-g (18%) sample of pure hexamethylbenzene was obtained.

Cycloaddition of 1,3-butadiene with 2-butyne using $Fe(COT)_2$ was by the same procedure as in the foregoing case. $Fe(COT)_2$ (40 mg), 2 ml of liquefied butadiene, and 1 ml of 2-butyne were charged, and the sealed vial was maintained 24 hr at room temperature. The vial was opened at −20° and the unreacted butadiene was vented off. The reaction mixture was dissolved in 20 ml of diethyl ether; the solution was washed with 0.1 N hydrochloric acid and with water and dried ($MgSO_4$). The ether was distilled, leaving 0.45 g (55%) of a high-boiling liquid (bp $\approx$ 140°), consisting essentially of 1,2-dimethyl-1,4-hexadiene. The identification was made by the vpc retention time and by the ir spectrum in comparison with the pure product.[13]

Cycloaddition of 1,3-Butadiene with Tolane Using the $FeCl_3$–(i-C_3H_7)MgCl–Etherate System. Synthesis of 1,2-diphenyl-1,4-cyclohexadiene was by the same procedure as in the foregoing cases, but charging was effected at −40° in the following order: 10 ml of diethyl ether (freshly distilled on $LiAlH_4$), 0.1 g of sublimed $FeCl_3$, 3 ml of liquefied butadiene, 1.7 g of tolane, and 1.5 ml of a 3.4 M solution of i-C_3H_7MgCl (Grignard) in diethyl ether. The sealed vial was maintained 48 hr at room temperature, and the brown reaction mixture was purified as described above. An aliquot (0.2 g) of the high-boiling residue ($\approx$2 g) was chromatographed in a silica gel column (30 × 1.5 cm) by eluting with n-heptane. The white crystals that collected after a first oily fraction were recrystallized from ethanol to yield 150 mg (68%) of pure product: mp 80–81°; uv max (Unicam SP 800, 230–450 nm range), 256 nm (log ϵ 3.83); ir (Perkin-Elmer 125), 695, 760, 1030, 1118 (aromatic C–H), 664, 1423, and 3030 cm^{-1} (*cis*-double bond); nmr (Varian HA, 100 Mc, room temperature, $CDCl_3$ solvent, TMS standard), δ 7.05 (s, 5, C_6H_5), 5.86 (t, 1, J = 2.7 Hz, —CH═), and 3.13 ppm (d, 2, J = 1.4 Hz, $-CH_2-$); mass spectrum (72 eV), m 232 (prevailing), 230 (aromatization product). Partial aromatization was observed also by vpc (C. Erba LAC 796, cyclohexamethanol succinate): o-diphenylbenzene as tail peak; main product retention time relative to diphenyl, 5.54 (200°).

Anal. Calcd for $C_{18}H_{16}$: C, 93.11; H, 6.89. Found: C, 93.3; H, 6.8; mol wt (Mechrolab), 234 ± 2.

Registry No.—2-Butyne, 503-17-3; tolane, 501-65-5; butadiene (1,3), 106-99-0; $FeCl_3$, 7705-08-0; FeA_3, 14024-18-1; i-PrMgCl, 1068-55-9; n-BuLi, 109-72-8; $Al(Et)_3$, 97-93-8; DPC, 17351-29-0.

Reaction of Methylmagnesium Iodide and Diethy 1,2-Cyclohexanedicarboxylates

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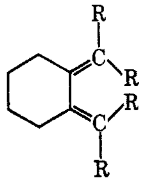
1,2-Diisopropylidenecyclohexane (I, R = CH_3)[1] has recently been obtained by photolysis of 1,1,3,3-tetramethyl-4,5,6,7-tetrahydro-2-indanone.[2] The preparation of this diene and its tetraphenyl analog (I, R = C_6H_5) were claimed earlier by Nazarov and Kuznetsov;[3] however, the physical properties reported for 1,2-diisopropylidenecyclohexane[3] are in almost perfect agreement with those of 1,2-diisopropylbenzene,[4] and we have not been able to reproduce their preparation of the tetraphenyl analog. In addition, our investigation of the products from the reaction of methylmagnesium iodide or methyllithium with the diethyl 1,2-cyclohexanedicarboxylates, which we report in this communication, has provided structural assignments which differ significantly from those reported by the Russian workers.[3]



I

Our work began with an examination of the reactions of diethyl 4-cyclohexene-*cis*-1,2-dicarboxylate. With a large excess (7.5 equiv) of methylmagnesium iodide, a good yield of *cis*-$\alpha,\alpha,\alpha',\alpha'$-tetramethyl-4-cyclohexene-1,2-dimethanol (II) was obtained, whereas the *cis*-

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[1] Inspection of Stuart–Briegleb molecular models of exocyclic dienes of type I where R is alkyl or aryl suggest that rotation about the C_1–C_2 bond should be restricted by interaction of adjacent R groups and should prevent chair–chair interconversion. If this is true, these dienes should be disymmetric and capable of resolution into their optical antipodes.

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[4] The Russian workers alleged to have obtained 1,2-cyclohexanedione and acetone by ozonolysis of this diene. Acetone was characterized as a 2,4-DNP derivative which was reported to melt at 195°. Authentic acetone 2,4-DNP melts at 125°.