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The Oligomerization of Isoprene by Cobalt or Iron Complex Catalysts

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The reaction of isoprene by the catalyst systems composed of cobalt(III) or iron(III) acetylacetonate, an electron donor, and triethylaluminum was studied. It was found that isoprene is selectively dimerized to form a mixture of 1, 5- and 2, 5-dimethyl-1, 5-cyclooctadiene by the catalyst prepared by the reaction of iron(III) acetylacetonate, 2, 2′-dipyridyl, and triethylaluminum. The intermediate complex of the reaction was then examined by studying the effects of the molar ratio of the catalyst components on the reaction or by the measurement of the electronic absorption spectra of the reaction solution. The reaction of butadiene with the catalyst systems described above was also carried out and compared with that of isoprene.

Several complex catalyst systems for the selective dimerization or trimerization of butadiene have been reported, most of them composed of first-row transition metal complexes and organometallic compounds. On the other hand, only a few complex catalyst systems for the dimerization or trimerization of isoprene[1] have been found, although various cyclic dimers of isoprene have been obtained by thermal or photosensitized reaction. It has now been found that isoprene is selectively dimerized to form a mixture of 1, 5- and 2, 5-dimethyl-1, 5-cyclooctadiene by the catalyst combining iron(III) acetylacetonate, triethylaluminum, and a proper bidentate electron donor such as 2, 2′-dipyridyl or *o*-phenanthroline. This paper will be concerned with the reaction of isoprene by the catalyst systems composed of cobalt(III) or iron(III) acetylacetonate, an electron donor, and triethylalumium, in particular, by the above-mentioned catalyst system. Moreover, the intermediate complex of the reaction will be discussed by studying the effects of the molar ratio of the catalyst components on the reaction and by analyzing the electronic absorption spectra of the reaction solution.

Experimental

Reagents.— Isoprene and 2, 3-dimethylbutadiene were dried over anhydrous calcium sulfate and distilled under an atmosphere of nitrogen.

Triethylaluminum (Ethyl Corp., U. S. A.) was used without further purification.

The electron donors were those of commercial reagents or were prepared by the usual methods.

Benzene was purified by conventional procedures.

Procedure.—Experiments were carried out in a 30-ml. glass tube, a 200-ml. glass autoclave, or a 100-ml. stainless autoclave. Benzene, isoprene and triethylaluminum were added in a dry nitrogen atmosphere.

In a typical reaction, 20 ml. of benzene, 10 ml. of isoprene, and 0.33 g. of triethylaluminum were added, in this order, to an autoclave which had been charged with 0.353 g. of iron(III) acetylacetonate and 0.156 g. of 2, 2′-dipyridyl. The autoclave was then heated at 90°C and stirred for 1 hr.

After the reaction, the solution was washed with dilute hydrochloric acid and with water, and dried over anhydrous sodium sulfate. Then the solution was fractionated by distillation. The dimers were isolated by fractional distillation at a reflux ratio of at least 1 : 6 in a rectifying column, or by preparative gas chromatography. For the analysis of the products, gas chromatography was also used.

Analysis.—*Gas Chromatography.*—The dimers of isoprene were analyzed by using a copper tube (3 m. long and 4 mm. in diameter) packed with polydiethylene glycol succinate on Diasolid (Nihon Kuromato, Ltd.). The conditions were as follows; column temperature, 110°C; flash evaporator temperature, 220°C; carrier gas (helium) speed, 30 ml./min. The isomers of dimethyl-1, 5-cyclooctadiene were detected by using a 3 m. β, β'-oxydipropionitrile column (column temperature, 124°C; flash evaporator temperature, 220°C; carrier gas speed, 30 ml./min.).

Infrared Spectra.—The infrared spectra of the products were taken with a Nihon-bunko double-beam spectrometer, Model 401-G.

Electronic Spectra.—The electronic spectra of the reaction solution were recorded by using 0.1 mm.-pathlength spacer cells on a Hitachi spectrometer Model EPS.

NMR Spectra.—The spectra were recorded on a Nihon Denshi apparatus JEOL Model 3H-60.

Results and Discussion

Structural Assignments of Products.—The products formed by the reaction of isoprene with a catalyst combining cobalt or iron acetylacetonate, an electron donor, and triethylaluminum are given in Table I. The product with a relative retention time below 3.7 based on benzene was supposed to be a dimer of isoprene.

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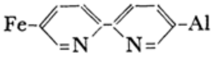
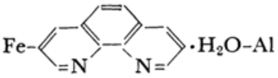
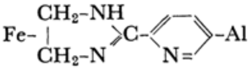
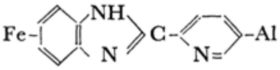
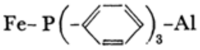
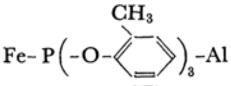
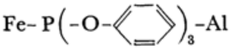
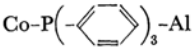
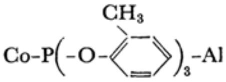
[1] L. I. Zaharkin, *Doklady Akad. Nauk, SSSR,* **131**, 1069 (1960); G. Wilke, *Angew. Chem.*, **75**, 10 (1963); L. I. Zaharkin, *Izv. Akad. Nauk, SSSR,* **1964**, 168.

Table I. Reaction products of isoprene by iron or cobalt complex catalysts

Catalyst	Products 1.6	2.3	2.7	3.0	3.7	6.0	6.3*	Polymer
Fe-Al		t	t	t	t			m
	s	s			l			
	t	s	t		m			
		t	t	t	s			m
								l
					t			
								l
								l
Co-Al	t	s			s	t	s	l
		t			t			
		t			t			

Abbreviations:
Fe: iron(III) acetylacetonate, Co: cobalt(III) acetylacetonate, Al: triethylaluminum
The yields of the products were indicated by the symbols l (above 50%), m (10—50%), s (1—10%), and t (below 1%).
* Relative retention time of product based on benzene
Reaction conditions:
Al/Fe: 3; Donor/Metal acetylacetonate: 1 (mole ratio); React. temp.: 90°C; React. time: 1 hr.

The analytical gas chromatography of reaction products formed by the catalyst prepared by the reaction of iron(III) acetylacetonate, 2, 2′-dipyridyl, and triethylaluminum showed three peaks, of which the relative retention times were 1.6, 2.3, and 3.7 respectively. Here, at present, these will be designated as A, B, and C respectively, in which C was the main product, the yields of A and B being low. The main product, C, was isolated by fractional distillation. The analytical results of C were as follows, where the values in parentheses are the theoretical values calculated for $C_{10}H_{16}$;

Molecular weight	138 (136)
Elementary analysis	C: 87.70%, H: 11.82% (C: 88.17%, H: 11.84%)
Refractive index	n_D^{20}: 1.4881
Boiling point	80°C/23 mmHg
Iodine value	350

The results of molecular weight determination, elementary analysis, and iodine value indicated that C had the formula of $C_{10}H_{16}$, with two double bonds; hence, it was considered a cyclodimer. Twelve cyclodimers of isoprene of $C_{10}H_{16}$ can be formulated; their structures may be grouped as six cyclobutenes, four cyclohexenes, and two cyclooctadienes. All of cyclobutenes and cyclohexenes contain one terminal vinyl or methylene group at least. The infrared spectrum of C (shown in Fig. 1), however, showed no bands characteristic of the group. Therefore, C was supposed to be 1, 5-dimethyl-1, 5-cyclooctadiene (I), or 2, 5-dimethyl-1, 5-cyclooctadiene (II), or a mixture of them. The infrared spectrum, the boiling point, and the refractive index of C were essentially identical with those of a mixture of I and II given

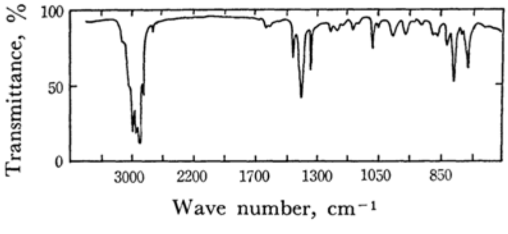


Fig. 1. Infrared spectrum of the fraction of b. p. 80°C/23 mmHg.

by Binder.[2] Furthermore, on the basis of the relative intensities of the bands in the infrared specturm at 1070 and 1093 cm^{-1} which have been considered to be characteristic of I and II respectively,[3] it was concluded that C was a mixture of I and II, and that II was the main constituent. These two isomers, I and II, were also detected by gas chromatography by using a β, β'-oxydipropionitrile column; here the ratio of II to I was determined to be about 4. On the other hand, the NMR spectrum of C (shown in Fig. 2) showed three resonances, at 8.3, 7.8, and 4.8 τ, which were assigned, respectively, to six methyl protons next to a double bond, eight methylene protons next to a double bond, and two ethylenic protons.

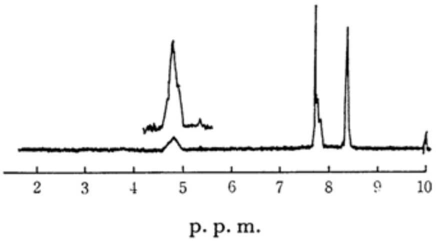
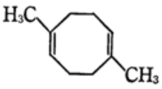
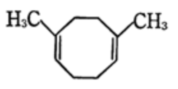


Fig. 2. NMR spectrum of the fraction of b. p. 80°C/23 mmHg.



(I)

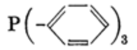
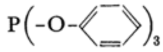
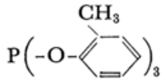
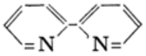
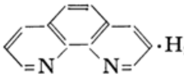
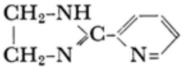
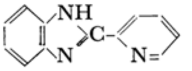


(II)

The boiling points of A and B were so near that their separation was difficult. As they were also formed in the case of thermal reaction, however, they were considered to be thermal dimers. The fraction with a b. p. of 75—77°C/23 mmHg was about 70% B and 30% C. By the infrared spectrum of the fraction, B was identified as 1-methyl-4-isopropenyl-1-cyclohexene or/and 2-methyl-4-isopropenyl-1-cyclohexene. The fraction with a b. p. of 69—71°C/23 mmHg was about 50% A and 50% B. The infrared spectrum of the fraction indicated that A was 1, 4-dimethyl-4-vinyl-1-cyclohexene or/and 2, 4-dimethyl-4-vinyl-1-cyclohexene.

The Effects of Electron Donors.—Table II shows the effects of electron donors upon the reaction of isoprene with the catalyst prepared by the reaction of iron(III) acetylacetonate and triethylaluminum. Isoprene did not react to the catalyst composed of iron(III) acetylacetonate, triphenylphosphine, and triethylaluminum, although the linear dimers are formed in the case of butadiene.[4] When triphenylphosphite or tri(*o*-tolyl)phosphite was added as a catalyst component, polymers were formed. The addition of a bidentate ligand such as 2, 2′-dipyridyl or *o*-phenanthroline gave the cyclodimers selectively, while the addition of a bidentate ligand such as 2(2′-pyridyl)imidazoline or 2(2′-pyridyl)benzimidazole led to the formation of polymers. These facts indicate that the reaction of isoprene by the catalyst composed of iron(III) acetylacetonate, an electron donor and triethylaluminum was greatly affected by the nature of the electron donor as a catalyst component.

TABLE II. EFFECTS OF ELECTRON DONORS UPON THE REACTION OF ISOPRENE BY THE CATALYST COMPOSED OF IRON(III) ACETYLACETONATE AND TRIETHYLALUMINUM

Donor	Conv. %	Yield of dimers, %	
none	30	t	
	9		
	74	t	polymer
	54	t	polymer
	100	92	
 ·H_2O	67	36	
	50	5	polymer
	100		polymer

Reaction conditions:
Al/Fe: 3; C_5H_8/Fe: 100; Donor/Fe: 1;
React. temp.: 90°C; React. time: 1 hr.

The Reaction of Isoprene by the Catalyst Composed of Iron(III) Acetylacetonate, 2, 2′-Dipyridyl and Triethylaluminum.—*The Effects of the Molar Ratio of the Catalyst Components.*—The effects of the molar ratio of 2, 2′-dipyridyl to iron(III) acetylacetonate on the reaction are shown in Fig. 3. The most active catalyst system for the cyclic dimerization was formed when one mole of 2, 2′-dipyridyl was added to one mole of iron(III) acetylacetonate. When more than one mole of 2, 2′-dipyridyl was added to one mole of iron(III) acetylacetonate, both the conversion of isoprene and the yield of the cyclic dimers decreased. The same phenomena had been observed in the cyclic dimerization of butadiene with the same catalyst system.[4] On the other hand, 2, 3-dimethyl-1, 3-butadiene did not react with the same catalyst.

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[2] J. L. Binder, K. C. Eberly and G. E. P. Smith, *J. Polymer Sci.*, **38**, 229 (1959).

[3] G. S. Hammond, *J. Org. Chem.*, **28**, 3302 (1963).

[4] M. Hidai, K. Tamai, Y. Uchida and A. Misono, This Bulletin, to be published.

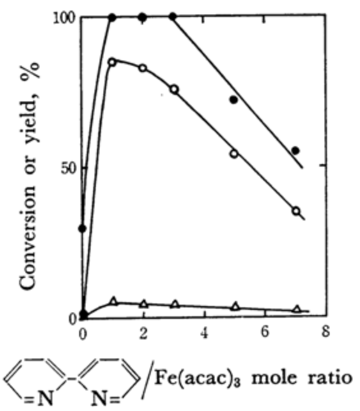


Fig. 3. Effect of molar ratio of 2, 2′-dipyridyl to iron(III) acetylacetonate.
●: Conversion of isoprene, %
○: Yield of 1, 5(2, 5)-dimethyl-1, 5-cycloocta-diene, %
△: Yield of 1(2)-methyl-4-isopropenyl-1-cyclohexene, %
Reaction conditions:
$AlEt_3/Fe(acac)_3$: 3; $C_5H_8/Fe(acac)_3$: 100;
Reactn. time: 1 hr.; Reactn. temp.: 90°C

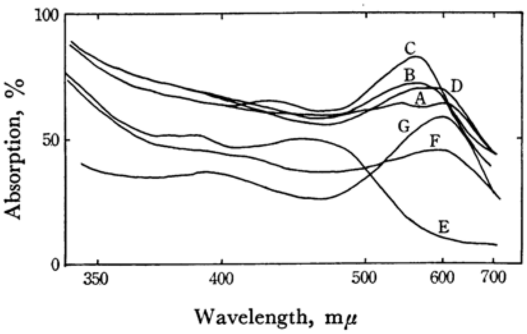


Fig. 4. Electronic absorption spectra of reaction solutions.
Molar ratios are as follows;
A: Fe : Dip : Al : Bz = 1 : 1 : 3 : 10^3
B: Fe : Dip : Al : IP : Bz = 1 : 1 : 3 : 70 : 10^3
C: Fe : Dip : Al : BD : Bz = 1 : 1 : 3 : 10^2 : 10^3
D: Fe : Dip : Al : DMBD : Bz = 1 : 1 : 3 : 70 : 10^3
E: Fe : Dip : Al : IP : Bz = 1 : 1 : 8 : 70 : 10^3
F: Fe : Dip : Al : IP : Bz = 1 : 8 : 3 : 70 : 10^3
G: Benzene solution of $Fe(dip)_2Et_2$[5] prepared by the reaction of $Fe(acac)_3$, 2, 2′-dipyridyl, and $AlEt_2(OEt)$ in ether
where
Fe: $Fe(acac)_3$, Dip: 2, 2′-dipyridyl, Al: $AlEt_3$,
Bz: benzene, IP: isoprene, BD: butadiene,
DMBD: 2, 3-dimethylbutadiene.

Figure 4 shows the electronic absorption spectra of the solution prepared by the reaction of iron(III) acetylacetonate, 2, 2′-dipyridyl, triethylaluminum and a diene monomer in various ratios at room temperature. The solution obtained by the reaction of iron(III) acetylacetonate, 2, 2′-dipyridyl, and triethylaluminum (molar ratio; 1 : 1 : 3) showed a maximum absorption peak at about 600 mμ and a dark blue color. This absorption peak, which was considered to be due to the charge transfer between the iron atom and 2, 2′-dipyridyl, shifted to about 550 mμ and the solution became purple when butadiene or isoprene was present. However, the shift was not observed when an excess of 2, 2′-dipyridyl was added.

These facts indicate that a dark blue complex is formed by the reaction of iron(III) acetylacetonate, 2, 2′-dipyridyl, and triethylaluminum, and that this blue complex is changed into a purple complex by the addition of butadiene or isoprene, in which the diene monomers besides 2, 2′-dipyridyl are coordinated to a low valent iron atom. When an excess of 2, 2′-dipyridyl is present, the ligands occupy all, or at least the greater part, of the coordinating sites of the low valent iron atom and, therefore, prevent the approach of the diene monomer. Thus, when an excess of 2, 2′-dipyridyl was present, the reaction of isoprene was depressed. On the other hand, the fact that the solution obtained by the reaction of iron(III) acetylacetonate, 2, 2′-dipyridyl, and triethylaluminum (molar ratio: 1 : 1 : 3) in the presence of 2, 3-dimethyl-1, 3-butadiene was dark blue indicates that the monomer is not coordinated to the low valent iron atom.

Figure 5 shows the effects of the molar ratio of triethylaluminum to iron(III) acetylacetonate on the reaction. When the molar ratio of triethylaluminum to iron(III) acetylacetonate was below 3, the reaction solution was purple and the cyclic

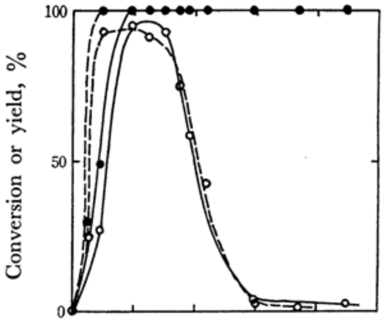
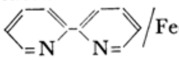


Fig. 5. Effect of molar ratio of triethylaluminum to iron(III) acetylacetonate.
●: Conversion of isoprene, %
○: Yield of cyclic dimers, %
——: Reactn. temp., 40°C
----: Reactn. temp., 50°C
Reaction conditions:



/$Fe(acac)_3$: 1; $C_5H_8/Fe(acac)_3$: 100;
Reactn. time: 1 hr.

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[5] A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida and A. Misono, *J. Am. Chem. Soc.*, **87**, 4652 (1965).

dimers of isoprene were formed selectively. However, when the molar ratio was above 6, the reaction solution turned reddish brown, as is shown in Fig. 4, and only polymers were formed.

The Effect of the Mixing Order of the Catalyst Components. — In the dimerization of butadiene with a cobalt complex catalyst or in the trimerization of butadiene with an iron complex catalyst, it has been reported that the order of mixing the catalyst components and butadiene had a great effect on the reaction.⁶⁾ The effects of the mixing order of the catalyst components on the formation of the cyclic dimers of isoprene or butadiene by the catalyst composed of iron(III) acetylacetonate, 2, 2′-dipyridyl, and triethylaluminum are shown in Table III. Evidently the rate of the formation of the cyclic dimers was greater when iron(III) acetylacetonate, 2, 2′-dipyridyl, isoprene or butadiene, and triethylaluminum were mixed in this order than when triethylaluminum was allowed to react with iron(III) acetylacetonate and 2, 2′-dipyridyl in the absence of isoprene or butadiene. These results indicate that when iron(III) acetylacetonate and 2, 2′-dipyridyl are reacted with triethylaluminum in the presence of the diene monomer, a purple complex, which is supposed to be an intermediate complex for the cyclic dimerization, is easily formed, while when iron(III) acetylacetonate, 2, 2′-dipyridyl, triethylaluminum, and the diene monomer are mixed in this order, the dark blue complex first formed by the reaction of iron(III) acetylacetonate, 2, 2′-dipyridyl and triethylaluminum does not easily react with the diene monomer to form the purple complex.

TABLE III. EFFECTS OF MIXING ORDER OF CATALYST COMPONENTS

Mixing order	Reactn. temp. °C	Reactn. time min.	Conv. %	Yield of cyclic dimers, %
Fe-Dip-Bz-IP-Al	50	60	100	96
Fe-Dip-Bz-Al-IP	50	60	92	88
Fe-Dip-Bz-BD-Al	50	240	73	45
Fe-Dip-Bz-Al-BD	50	300	30	25

Reaction conditions:
Fe/Al: 3; Dip/Fe: 1; IP/Fe: 100; BD/Fe: 200 (mole ratio)

A Comparison of Isoprene and Butadiene.— It has been reported that butadiene is dimerized to form the linear dimers by the cobalt complex catalyst prepared by the reaction of cobalt(III) acetylacetonate and triethylaluminum or by the iron complex catalyst prepared by the reaction of iron(III) acetylacetonate, triphenylphosphine, and triethylaluminum.⁴·⁶⁾ However, in these catalyst systems, the reactivity of isoprene was not so great as butadiene and linear dimers were not formed. On the other hand, when the catalyst composed of iron(III) acetylacetonate, 2, 2′-dipyridyl, and triethylaluminum was used, with which butadiene is dimerized to form the cyclic dimers, isoprene reacted more easily than butadiene and the cyclic dimers were similarly formed. These facts indicate that the coordination state of a diene monomer to a low valent cobalt or iron tom in the case of the formation of linear dimers is different from that in the case of the formation of cyclic dimers, and that isoprene is not likely to have a coordination state giving linear dimers.

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6) T. Saito, T. Ohno, Y. Uchida and A. Misono, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **66**, 1099 (1963); M. Hidai, Y. Uchida and A. Misono, This Bulletin, **38**, 1243 (1965).