reactive acetylene (at the same temperature) was injected through the vaccine cap with a hypodermic syringe. Disappearance of the added acetylene was determined by infrared analysis of the C≡C stretching band in the solution after an additional 2-hr. period. The disubstituted acetylene was recovered from the reaction mixture along with the usual polymer products from the added acetylene, when formed.

Mathematical Analysis of Deuterium Isotope Effect in the Trimerization of 1-Heptyne.—The reactions considered in the polymerization process were

$$C + 2X \xrightarrow{k_r} Z \qquad (8)$$

$$C + 2Y \xrightarrow{k_r} Z \qquad (9)$$

$$C + X + Y \xrightarrow{k_r} Z \qquad (10)$$

$$C + Y + X \xrightarrow{k_r} Z \qquad (11)$$

$$Z + X \xrightarrow{k_H} \text{Product} + C \qquad (12)$$

$$Z + Y \xrightarrow{k_D} \text{Product} + C \qquad (13)$$

where

X = a measure of hydrogen compound concentration
Y = a measure of deuterium compound concentration
Z = a measure of intermediate concentration
C = a measure of "active" catalyst concentration
k_H, k_D = rate constants for the rate-determining step involving reaction with an undeuterated and deuterated molecule, respectively
k_r = rate constant for the formation of intermediate Z

The assumption was made that the product formed was exclusively trimer and that only one hydrogen atom was transferred in the rate-determining step. These reactions then led to the differential equations

$$-\frac{dX}{dt} = k_HZX + k_rC(2X^2 + 2XY) \qquad (14)$$

$$-\frac{dY}{dt} = k_DZY + k_rC(2XY + 2Y^2) \qquad (15)$$

$$-\frac{dZ}{dt} = k_HZX + k_DZY - k_rC(X^2 + 2XY + Y^2) \qquad (16)$$

At steady state $dZ/dt = 0$. Solution of equation 16 and the subsequent substitutions $V = Y/X$ and $K = k_H/k_D$ into the ratio of equations 14 and 15 resulted in expression 17 in V, X, and K,

$$2 \ln (V + 1) + \frac{3K}{1 - K} \ln V + \ln S = \ln X \qquad (17)$$

where S = a constant of integration. With the initial condition ($t = 0$) that $V = X = 1$, the final theoretical relationship was

$$2 \ln (V + 1) + \frac{3K}{1 - K} \ln V - 1.38629 = \ln X \qquad (18)$$

In Table IV are shown the values of V predicted from the model chosen. The experimental data were first fitted to equation 17 by least squares to obtain estimates of K and S. The resulting estimate of S was found to be not significantly different from the theoretical value. Therefore, the data were refitted to equation 18 for which the best value of K was 2.56 with a 95% confidence interval of ±0.46.

Infrared analyses were performed on a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. Ultraviolet spectra were determined on a Cary Model 14 ultraviolet spectrophotometer.

Acknowledgment.—The authors wish to thank Mr. A. L. Stockett of the Mathematical Analysis Section for the numerical solution of the equations describing the deuterium isotope effects.

Some Reactions of Monoölefins with Iron Carbonyls

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The treatment of monoölefins with iron carbonyls leads to isomerization. The effects of olefin structure and solvent upon the reaction are discussed, and a mechanism for the reaction is suggested.

Recent interest in reactions of iron carbonyl and its derivatives with nonconjugated diolefins[1,2] prompts us to report some of our data regarding reactions of iron carbonyls with monoölefins. It has been shown that the iron carbonyl hydrides are active catalysts for hydrogenation and isomerization of olefins,[3,4] as are the cobalt carbonyl hydrides,[5,6] and it was noted that treatment of 1-octene with iron pentacarbonyl gave a mixture of internal isomers.[7] We have investigated the geometrical and positional isomerization occurring when monoolefins of various structures are heated with iron carbonyls.

Terminal olefins are rapidly converted to mixtures of internal isomers when heated with iron carbonyls.

Table I compares the experimental values for isomer distribution of hexenes after heating with 0.5 mole % triiron dodecacarbonyl with the thermodynamic equilibrium values calculated by stand-

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(1) R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

(2) R. Pettit and J. E. Arnet, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

(3) H. W. Sternberg, R. Markby, and I. Wender, *ibid.*, **78**, 5704 (1956).

(4) H. W. Sternberg, R. Markby, and I. Wender, *ibid.*, **79**, 6116 (1957).

(5) R. F. Heck and D. S. Breslow, *ibid.*, **83**, 4023 (1961).

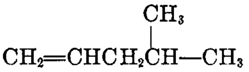
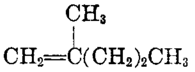
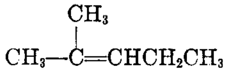
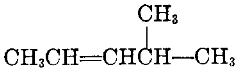
(6) I. Wender, S. Metlin, S. Ergun, H. W. Sternberg, and H. Greenfield, *ibid.*, **78**, 5401 (1956).

(7) F. Asinger and O. Berg, *Ber.*, **88**, 445 (1955).

TABLE I

COMPARISON OF EXPERIMENTAL AND THEORETICAL ISOMER DISTRIBUTIONS

	% $CH_2{=}CH(CH_2)_3CH_3$	% *cis*- $CH_3CH{=}CH(CH_2)_2CH_3$	% *trans*- $CH_3CH{=}CH(CH_2)_2CH_3$	% $CH_3CH_2CH{=}CHCH_2CH_3$
Exp.[a]	1.6	16.2	57.6	25
Calcd.	1	20	47	32

	 $CH_2{=}CHCH_2\overset{\overset{CH_3}{\vert}}{C}H{-}CH_3$	 $CH_2{=}\overset{\overset{CH_3}{\vert}}{C}(CH_2)_2CH_3$	 $CH_3{-}\overset{\overset{CH_3}{\vert}}{C}{=}CHCH_2CH_3$	 $CH_3CH{=}CH\overset{\overset{CH_3}{\vert}}{C}H{-}CH_3$
Exp.[b]	0	13	74	13
Exp.[c]	0	13	74	13
Calcd.	0.07	12	79	9.4

[a] 1-Hexene, refluxed 4 hr. [b] 4-Methyl-1-pentene, refluxed 19 hr. [c] 2-Methyl-1-pentene, refluxed 19 hr.

ard methods[8] from free energies of formation at 25°.[9]

Clearly, the experimental data parallel the trends of the theoretical values.

The disubstituted internal olefins formed are found mainly in the *trans* configuration, and in the case of branched-chain olefins, trisubstituted isomers are preferentially formed. For instance, 2-methyl-1-pentene is found in much larger amounts in the products of methylpentene isomerization than is 4-methyl-1-pentene.

The results of some other reactions are shown in Table II. Internal olefins react much more slowly with iron carbonyls than do terminal olefins, and trisubstituted olefins are even less reactive. While 1-hexene was essentially completely converted to 2-hexene and 3-hexene within two hours, under the same conditions 74% of a sample of (82% *cis*) 2-hexene was unchanged in nineteen hours. *Cis* olefins are isomerized more readily than their *trans* isomers, as is shown by the case of 4-methyl-2-pentene. The trisubstituted internal olefin 2-methyl-2-pentene appeared to be unaffected under our isomerization conditions. These observations on the relative reactivity of types of olefins parallel those made by other workers studying related reactions involving π-complex formation.[5,6] It should be noted that occasionally the iron carbonyl–olefin reactions produce small amounts of less volatile, unidentified substances.

Pettit and Arnet reported that heating 4-vinyl-1-cyclohexene with iron pentacarbonyl gave a mixture of conjugated diene–iron tricarbonyl compounds.[2] In the course of our studies we found that vinylcyclohexane was isomerized by treatment with triiron dodecacarbonyl to a mixture of 1-ethyl-1-cyclohexene and ethylidenecyclohexane, while under the same conditions a mixture of 4-methyl-1-cyclohexene and 3-methyl-1-cyclohexene showed no conversion to the more highly substituted isomer, 1-methyl-1-cyclohexene. These observations make it likely that the C_8H_{12} isomers in the complexes earlier isolated[2] contain both double bonds within the ring.

The actual isomerization process is probably catalytic, since only 0.005 mole of iron carbonyl per mole of 1-hexene caused almost complete disappearance of the terminal olefin in two hours, but thermal decomposition of the iron carbonyl prevents its use in exceedingly small quantities. A temperature above 100° is required for reaction with iron pentacarbonyl, and a temperature above 60° for reaction with triiron dodecacarbonyl. Thus, the boiling point of the olefin determines the choice of iron carbonyl for reaction. For example, 1-hexene (b.p. 64°) is best isomerized with triiron dodecacarbonyl, whereas with 1-octene (b.p. 121°) iron pentacarbonyl may be conveniently used. The use of pressure vessels to raise the reaction temperature is ineffective since the isomerization is apparently inhibited by carbon monoxide pressure. In some cases the use of a higher boiling inert solvent to raise the reaction temperature is helpful (Tables III, IV).

An interesting aspect of these studies is the effect of additional solvent species upon the reaction, also briefly noted by workers on related topics.[6] Addition of small amounts of polar substances such as acetone, 1,2-dimethoxyethane, or ethanol appears to promote isomerization whereas the presence of acetic acid or benzoyl chloride strongly inhibits isomerization (Tables III, IV, V). The addition of a small amount of pyridine permits the use of iron pentacarbonyl with lower boiling olefins (see Experimental).

We have noted that when an iron carbonyl and an olefin, either internal or terminal, are heated in carbon tetrachloride, some polymerization may occur, but the main reaction is addition of carbon tetrachloride to the double bond. The iron chloride-catalyzed free radical addition of carbon tetrachloride to olefins has recently been described.[10] The reaction of carbonyls of chromium, molybdenum, tungsten, and iron with polyhalogenated organic compounds has been used to initiate the free radical telomerization of ethylene

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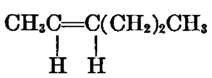
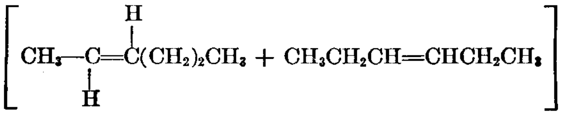
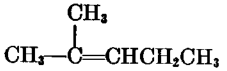
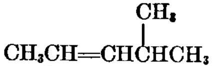
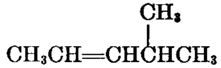
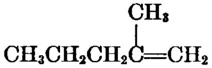
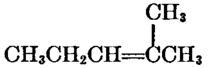
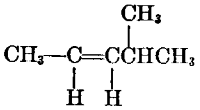
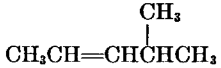
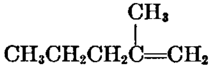
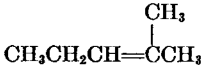
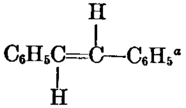
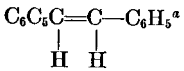
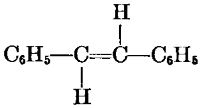
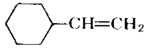
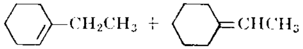
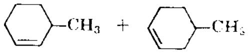
(8) F. D. Rossini, "Chemical Thermodynamics," John Wiley & Sons, Inc., New York, N.Y., 1950, p. 439.

(9) Selected Values of Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44, table 23-2-(5.1201).

(10) M. Asscher and D. Vofsi, *Chem. Ind.* (London), 209 (1962).

TABLE II
REACTIONS OF SOME MONOÖLEFINS WITH $Fe_3(CO)_{12}$

Starting olefin	$\frac{[Fe_3(CO)_{12}]}{[Olefin]}$	Time refluxed, hr.	Product mixture
(82% *cis*) $CH_3CH{=}CH(CH_2)_2CH_3$	0.005	19	74%  $CH_3\underset{H}{C}{=}\underset{H}{C}(CH_2)_2CH_3$ 25%  $\left[CH_3-\underset{H}{C}{=}\overset{H}{C}(CH_2)_2CH_3 + CH_3CH_2CH{=}CHCH_2CH_3\right]$
 $CH_3-\overset{CH_3}{C}{=}CHCH_2CH_3$	.005	16	No change
 $CH_3CH{=}CH\overset{CH_3}{C}HCH_3$ (largely *trans*)	.005	16	95%  $CH_3CH{=}CH\overset{CH_3}{C}HCH_3$ 2%  $CH_3CH_2CH_2\overset{CH_3}{C}{=}CH_2$ 2%  $CH_3CH_2CH{=}\overset{CH_3}{C}CH_3$
 $CH_3-\underset{H}{C}{=}\underset{H}{C}\overset{CH_3}{C}HCH_3$	.005	16	12%  $CH_3CH{=}CH\overset{CH_3}{C}HCH_3$ 12%  $CH_3CH_2CH_2\overset{CH_3}{C}{=}CH_2$ 77%  $CH_3CH_2CH{=}\overset{CH_3}{C}CH_3$
 $C_6H_5\underset{H}{C}{=}\overset{H}{C}-C_6H_5{}^a$	.07	22	No change
 $C_6C_5\underset{H}{C}{=}\underset{H}{C}-C_6H_5{}^a$	.07	22	 $C_6H_5-\underset{H}{C}{=}\overset{H}{C}-C_6H_5$
	.006	19	
	.008	22	No change

[a] Cyclohexane solution.

TABLE III

REACTION OF *cis*-2-PENTENE (95%) WITH $Fe_3(CO)_{12}$

Solvent	$\frac{[Fe_3(CO)_{12}]}{[Pentene]}$	Time refluxed, hr.	% *trans*-2-pentene
None	0.004	16	11
50% heptane	.008	23	69
5% acetone	.005	22	46

TABLE IV

REACTION OF 2-HEXENE WITH $Fe_3(CO)_{12}$[a]

Solvent	$\frac{[Fe_3(CO)_{12}]}{[Hexene]}$	Time refluxed, hr.	% 1-hexene	% *cis*-2-hexene	% *trans*-2-hexene	% 3-hexene
Starting material	0	0	0	82.4	10.8	1.0
None	0.006	19	1.3	61.7	26.5	7.5
7% acetone	.006	23	1.6	31.5	43.6	13.9
98% heptane	.20	3	...	20	70	10

[a] Other impurities make up to 100%.

TABLE V

REACTION OF 1-HEXENE (99%) WITH $Fe_3(CO)_{12}$

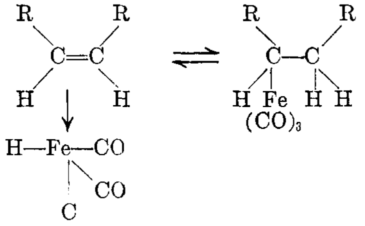
Solvent	$\frac{[Fe_3(CO)_{12}]}{[Hexene]}$	Time refluxed, hr.	% 1-hexene	% *cis*-2-hexene	% *trans*-2-hexene	% 3-hexene
None	0.005	4	1.6	16.2	57.6	24.6
9% acetone	.008	6	1.7	16.8	53.3	26.7
9% C_6H_5COCl	.008	22	55.8	8.3	24.3	11.6

with the halogenated compound[11–13] and the free radical polymerization of vinyl monomers.[14]

It is difficult to formulate mechanisms for the olefin isomerizations[1–7] catalyzed by iron or cobalt carbonyls which do not involve formation of a metal–hydrogen bond, and the carbonyl hydrides of these metals are easily formed.[15,16] Molybdenum hexacarbonyl, which was found to be inactive in producing conjugated from nonconjugated diolefins,[2] yields carbonyl hydrides only after relatively drastic treatment.[15,16] Nonetheless, we have found that refluxing octene-1 may be converted by molybdenum hexacarbonyl to a mixture of internal isomers. This observation suggests the formation of a molybdenum–hydrogen bond under relatively mild conditions.

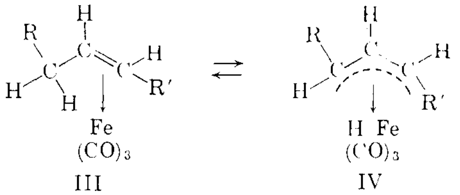
As the iron carbonyl hydrides are known to be potent agents for the isomerization of olefins,[3,4,17] the active species in the isomerizations catalyzed by the unsubstituted metal carbonyls probably are iron carbonyl hydrides. The solvent effects noted in this work further this hypothesis, since the bases which promote isomerization are known to promote disproportionation of iron carbonyls to mixtures containing the protonatable carbonyl anions.[16] Indeed, the reaction mixtures containing pyridine, a ketone, ether, or alcohol exhibit the characteristic red color of iron carbonyl anions.

The mechanism of these reactions is probably similar to those proposed for other metal carbonyl hydride-catalyzed isomerizations,[5,17] involving at some stage formation of a metal carbonyl hydride–olefin π-complex (I) in equilibrium with a σ-alkyl metal compound (II). In this way both geometrical and positional isomerization could easily occur.



(I) (II)

An alternative mechanism is one involving initial formation of an olefin–iron tricarbonyl complex (III), followed by abstraction of the allylic hydrogen to form a π-allyl iron carbonyl hydride complex (IV), in which rearrangement of the double bond could take place.



III IV

A π-butenyl iron carbonyl chloride complex has been isolated,[18] and π-allyl complexes of other transition metals are well known.[19]

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[11] R. X. Freydlina and A. B. Belyavsky, *Dokl. Akad. Nauk SSSR*, **127**, 1027 (1959).

[12] R. X. Freydlina and A. B. Belyavsky, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 177 (1961).

[13] A. N. Nesmeyanov, R. K. Freydlina, E. C. Chukovskaya, R. G. Petrova, and A. B. Belyavsky, *Tetrahedron*, **17**, 61 (1962).

[14] C. H. Bamford and C. A. Finch, *Proc. Chem. Soc.*, 110 (1962).

[15] M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

[16] W. Hieber, W. Beck, and G. Braun, *ibid.*, **72**, 795 (1960).

[17] H. W. Sternberg and I. Wender, International Conference on Coordination Chemistry, Special Publication No. 13, The Chemical Society, London, 1959, p. 53.

[18] F. J. Impastato and K. G. Ihrman, *J. Am. Chem. Soc.*, **83**, 3726 (1961).

[19] For an introduction to the extensive literature on such compounds see W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *ibid.*, **83**, 1601 (1961).

The two suggested routes are closely related and ample analogy exists for each. Of course, for the case of stilbene the latter mechanism is impossible and another source of hydrogen is required, possibly from impurities in the solvent or triiron dodecacarbonyl. Both mechanisms require π-complex formation, and substitution of electron-withdrawing groups on the double bond might be expected to lower its donor abilities and therefore its tendency to form the essential π-complex. Indeed, *cis*-1,2-dichloroethylene has not been successfully isomerized by us using iron carbonyl catalysts.

It is of interest that the double bond "migrates past" unreactive olefins to give other species. Thus, 2-methylpentenes are formed from 4-methyl-1-pentene, although *trans*-4-methyl-2-pentene is exceedingly difficult to isomerize; and 1-hexene is converted to 3-hexene, despite the unreactivity of 2-hexene. Formation of the initial π-complex seems to be the rate-determining step in these reactions, and rearrangement occurs within the complexed species without requiring formation of the intermediate olefins.

Experimental

Reagents.—The olefins used were commercial products (99% pure grade, when available) of the Phillips Petroleum Co., except for 1-hexene and *cis*-stilbene, supplied by Matheson, Coleman and Bell Co., and vinylcyclohexane, supplied by K and K Laboratories, Inc. Iron pentacarbonyl was obtained from Antara Chemical Co. and molybdenum hexacarbonyl from Climax Molybdenum Co. Triiron dodecacarbonyl was prepared by a method based on that of Hieber.[20]

Analytical.—The olefinic products and starting materials were analyzed by vapor phase chromatography, and retention times were compared with those of the pure compounds. Peak areas were determined using a Perkin–Elmer printing integrator. Routine analyses used a 21-ft. column of Adol-40 on Chromosorb at 50° with 15 p.s.i. helium as carrier gas. Crucial runs were checked using a 300-ft. squalane capillary column. Elemental analyses were performed by the Analytical Research Division of this Company. Infrared spectra were taken on a Beckman IR-5 instrument, and the C—H deformation frequencies and C=C stretching frequencies were correlated with the type of olefin present.[21]

Typical Procedure.—Reactions were ordinarily carried out by refluxing the olefins and metal carbonyls alone, or in the presence of another solvent, under nitrogen for from 2 to 24 hr. Some examples follow.

(1) **1-Hexene.**—A mixture of 25 ml. (200 mmoles) of 1-hexene with 0.5 g. (1 mmole) of triiron dodecacarbonyl was refluxed under nitrogen. Samples of 3-ml. volume were withdrawn by syringe at intervals, distilled at 0° under reduced pressure, and analyzed by infrared and v.p.c. (results in Table I).

(2) **1-Octene and Molybdenum Hexacarbonyl.**—A mixture of 25 ml. (160 mmoles) of 1-octene with 1.32 g. (5 mmoles) of molybdenum hexacarbonyl was refluxed under nitrogen for 21 hr. The cooled mixture was filtered. The infrared spectrum of the filtrate showed mainly *trans* internal olefin, with some *cis* and terminal olefinic groups present.

(3) **Use of Pyridine with Iron Pentacarbonyl.**—A mixture of 5 ml. (38 mmoles) of iron pentacarbonyl with 20 ml. of 1-hexene (160 mmoles) and 2 ml. (25 mmoles) of pyridine was refluxed under nitrogen for 17 hr. The cooled mixture was filtered, giving a pyrophoric residue and a red filtrate, which was distilled at 0° to give a colorless liquid. V.p.c. analysis showed the composition to be 68% 1-hexene, 5% *cis*-2-hexene, 24% hexene-3 and *trans*-hexene-2, and 3% high boiling impurities.

(4.) **Inhibition of Reaction by Carbon Monoxide Pressure.**—A 150-ml. steel bomb was charged with 15 ml. of heptane, 15 ml. (120 mmoles) of 2-hexene, and 0.7 g. (14 mmoles) of triiron dodecacarbonyl. The bomb was sealed, cooled to −196°, evacuated, and heated at 90° for 17 hr. Filtration of the cooled mixture gave a clear liquid showing in infrared and v.p.c. analysis virtually no change from the starting material.

(5.) **Vinylcyclohexane.**—A mixture of 20 ml. (140 mmoles) of vinylcyclohexane with 0.4 g. (0.8 mmoles) of triiron dodecacarbonyl was refluxed under nitrogen for 19 hr. Filtration of the cooled mixture followed by distillation gave a colorless liquid. Infrared analysis indicated the absence of vinylic double bonds and the presence of RR′C=CHR″ groups. V.p.c. analysis showed the presence of two substances of similar retention times. The nuclear magnetic resonance spectrum (Varian A-60 spectrometer) was consistent with the presence of ethylidene cyclohexane and 1-ethyl-1-cyclohexene.

(6.) **Use of Carbon Tetrachloride with Triiron Dodecacarbonyl.**—A mixture of 20 ml. (160 mmoles) of 1-hexene with 20 ml. (210 mmoles) of carbon tetrachloride and 4.0 g. (8 mmoles) of triiron dodecacarbonyl was refluxed under nitrogen for 4.5 hr. After filtration of the cooled mixture to remove a white solid, all material volatile at room temperature under the vacuum of a water aspirator was distilled. V.p.c. analysis showed only carbon tetrachloride with a trace of 1-hexene to be present. The remainder of the product was distilled at 60°/(0.1 mm.) to give a clear, colorless liquid. Found: C, 36.70; H, 5.36; Cl, 59.66. $C_7H_{12}Cl_4$ requires: C, 35.3; H, 5.0; Cl, 59.7.

(7) ***cis*-Stilbene.**—A mixture of 1.0 g. (5.6 mmoles) of *cis*-stilbene in 25 ml. of cyclohexane with 0.2 g. (0.4 mmole) of triiron dodecacarbonyl was refluxed under nitrogen for 22 hr. The mixture was cooled in Dry Ice and filtered, giving white crystals. Evaporation of the filtrate gave more crystals. The crystals had infrared spectra identical with that of *trans*-stilbene. No conversion to *trans*-stilbene was detected in the infrared spectrum when *cis*-stilbene was merely refluxed in cyclohexane.

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