to reflux and glpc analysis showed, after 15 min, **3** (60%), **4** (36%), indan **6** (0%); after 2 hr, **3** (14%), **4** (70%), **6** (6%); after 3 hr, **3** (10%), **4** (73%), **6** (7%); after 6 hr, **3** (0%), **4** (68%), **6** (7%).

Additional boron trifluoride etherate (0.260 g, 1.82 mmol) was added to the refluxing solution. Glpc analysis showed a steady decrease in **4** to 18% yield after 13.5 hr with no detectable increase in the amount of indan formation.

With *p*-Toluenesulfonic Acid in Glacial Acetic Acid.—1-(*o*-Hydroxymethylphenyl)cycloheptanol (**2**) (0.270 g, 1.23 mmol), *p*-toluenesulfonic acid monohydrate (0.0534, 0.281 mmol), an internal standard *n*-heptadecane (0.0563 g), and 8 ml of glacial acetic acid were added to a 50-ml two-neck round-bottom flask equipped with magnetic stirrer, condenser, and nitrogen inlet. The solution was heated to reflux temperature and the reaction process was followed by glpc analysis (5 ft × 0.25 in. 20% DC 710 on 60–80 mesh Chromosorb W, 210°, 60 ml/min He) with the following results: after 1 hr, **3** (68%), **4** (31%); after 3 hr, **3** (51%), **4** (40%). No indan by-product (**6**) was observed by glpc.

Reaction with Sulfuric Acid in Glacial Acetic Acid.—Concentrated sulfuric acid (0.09 g, 0.92 mmol) was added to a solution of *o*-(1-cycloheptanol) benzyl alcohol **2** (0.135 g, 0.610 mmol), *n*-heptadecane (0.0563 g) (internal standard) and 8 ml of acetic acid at the reflux temperature. Glpc analysis (5 ft 0.25 in. 20% DC 710 on 60–80 mesh Chromosorb W, 210°, 60 ml/min He) showed, after 5 hr, **3** (20%), **4** (60%); after 17 hr, **3** (0%), **4** (73%). None of the side product **6** was detected by glpc.

Registry No.—**2**, 34219-85-7; **3**, 32921-59-8; **4**, 34219-87-9; **6**, 34219-89-1; 6,7,8,9,10,11,12-heptahydro-5*H*-cyclonone[*a*]indene, 34219-88-0; 3-phenylindene, 1961-97-3

Homogeneous Hydrogen-Transfer Reactions Catalyzed by Tricarbonylchromium Complexes. Hydrogenation of Trienes[1]

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Hydrogenating 1,3,5-cycloheptatriene with methyl benzoate-$Cr(CO)_3$ yields a mixture of 1,3-cycloheptadiene and cycloheptene. The formation of 1,3- instead of 1,4-cycloheptadiene is in contrast to the results obtained with acyclic conjugated trienes. Deuteration experiments rule out 1,6 addition and support a mechanism involving 1,4 reduction followed by rapid isomerization of 1,4- to 1,3-cycloheptadiene (1,3-hydrogen-deuterium shift). Catalytic hydrogenation of *trans*-1,3,5-hexatriene with methyl benzoate-$Cr(CO_3)$ yields *cis*-1,4-hexadiene as the most important intermediate, the product expected from 1,4 addition. Hydrogenation of *cis*-1,3,5-hexatriene gives mainly cyclohexene. This product is derived from 1,3-cyclohexadiene formed by thermal cyclization of the cis hexatriene.

The homogeneous hydrogenation of unsaturated compounds continues to be the subject of intensive investigation. A high degree of selectivity is probably the most important practical characteristic of homogeneous hydrogenation catalysts.[3] Our studies of the catalytic activity of arene-$Cr(CO)_3$ complexes have demonstrated a selectivity approaching 100% in the hydrogenation of 1,3 and 1,4 dienes to monoenes.[4] Selectivity, kinetic, and deuterium tracer studies[4c,5] have provided ample evidence for 1,4 addition of hydrogen as the dominant mechanism of reduction catalyzed by these arene-$Cr(CO)_3$ complexes. With 1,4 dienes and monoenes, double-bond isomerization by 1,3-hydrogen shift was indicated.[5b]

Hydrogenation of methyl β-eleostearate (*all-trans*-9,11,13-octadecatrienoate) with these complexes yielded the diene products expected from 1,4 addition (*trans*-9,*cis*-12- and *cis*-10,*trans*-13-octadecadienoates).[6] With α-eleostearate (*cis*-9,*trans*-11,*trans*-13-octadecatrienoate) stereoselective 1,4 reduction producing up to 60% linoleate (*cis*-9,*cis*-12-octadecadienoate) was observed, but concurrent isomerization to β-eleostearate yielded also the corresponding cis,trans-1,4-diene products. This paper reports an extension of these studies to the hydrogenation of 1,3,5-cycloheptatriene and 1,3,5-hexatriene.

Results and Discussion

1,3,5-Cycloheptatriene.—Hydrogenations and deuterations were catalyzed by methyl benzoate-$Cr(CO)_3$ as in earlier work.[4c,5] Figure 1 plots results of kinetic runs with H_2 and D_2. 1,3-Cycloheptadiene was the main initial product detected by glc. Cycloheptene was formed in only minor amounts at 160°, but at 175° it was formed in significant amounts after 1,3-cycloheptadiene reached a maximum concentration of 80%. On the basis of previous work,[5] no significant kinetic isotopic effect would be expected. Identification of 1,3-cycloheptadiene by glc was confirmed by uv and ^1H nmr analyses of the hydrogenation products. That there was no 1,4-cycloheptadiene in the products was demonstrated by the absence of resonance corresponding to the α,α-methylene proton ($C{=}CCH_2C{=}C$) on C-3 (τ 7.20).

The formation of 1,3- instead of 1,4-cycloheptadiene

(1) Presented in part at the symposium "Homogeneous Catalysis by Organometallic Compounds," Division of Inorganic Chemistry, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Paper 72.

(2) A laboratory of the Northern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) (a) J. E. Lyons, L. E. Rennick, and J. L. Burmeister, *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 2 (1970); (b) A. Andreetta, F. Conti, and G. F. Ferrari, in "Aspects of Homogeneous Catalysis," Vol. I, R. Ugo, Ed., Carlo Manfredi, Milan, Italy, 1970, p 204; (c) E. N. Frankel and H. J. Dutton, in "Topics in Lipid Chemistry," Vol. I, F. D. Gunstone, Ed., Logos Press, London, 1970, p 206.

(4) (a) M. Cais, E. N. Frankel, and R. A. Rejoan, *Tetrahedron Lett.*, 1919 (1968); (b) E. N. Frankel and F. L. Little, *J. Amer. Oil Chem. Soc.*, **46**, 256 (1969); (c) E. N. Frankel and R. O. Butterfield, *J. Org. Chem.*, **34**, 3930 (1969).

(5) (a) E. N. Frankel, E. Selke, and C. A. Glass, *J. Amer. Chem. Soc.*, **90**, 2446 (1968); (b) *J. Org. Chem.*, **34**, 3936 (1969).

(6) (a) Paper 72;[1] (b) E. N. Frankel and F. L. Thomas, *J. Amer. Oil Chem. Soc.*, **49**, 70 (1972).

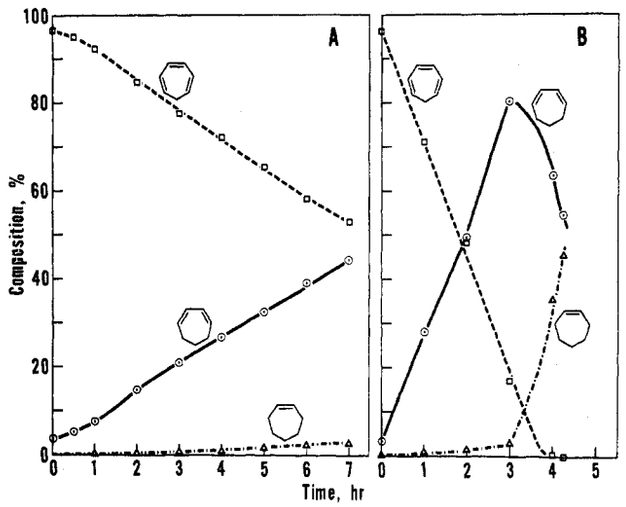
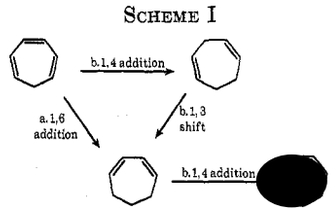


Figure 1.—Catalytic hydrogenation and deuteration of 1,3,5-cycloheptatriene with methyl benzoate-$Cr(CO)_3$: (A) run 1, 9.5 mmol of substrate, 0.5 mmol of catalyst, 50 ml of *n*-hexane, 160°, 30 atm of H_2; (B) run 2, 0.2 mol of substrate, 0.005 mol of catalyst, no solvent, 175°, 30 atm of D_2.

from 1,3,5-cycloheptatriene is in contrast to methyl eleostearate in which 1,4-diene fatty esters are the only initial products of hydrogenation with $Cr(CO)_3$ complexes.[6] Two possible routes can be considered for 1,3,5-cycloheptatriene, namely, (a) 1,6 addition or (b) 1,4 addition followed by rapid isomerization of 1,4- to the more stable 1,3-cycloheptadiene (Scheme I). It has been shown[7] that the 1,3 isomer represents

SCHEME I



nearly 100% of the equilibrium mixture of cycloheptadienes. The internuclear C_1–C_6 distance of the triene system (2.5 Å) and the C_1–C_4 distance of the 1,3-diene system (3.0 Å) of 1,3,5-cycloheptatriene are within 0.5 Å of each other in a model. Therefore, 1,6 addition (a) is not an unlikely path in a cyclic conjugated triene. Deuteration experiments were carried out to examine the two alternative reduction routes (a and b) in greater detail.

The products of run 2 (Figure 1) were separated by preparative glc and the fractions were analyzed at two levels of reduction. Mass spectral analyses showed the deuteration mixture to consist of cycloheptatriene-d_0, cycloheptadiene-d_2, and cycloheptane-d_4. The absence of deuterated cycloheptatriene species after partial reduction demonstrates that no exchange occurs before addition. The absence of d_1 and d_3 species in the reduced products indicates further that no scrambling of deuterium occurred after they are formed. If exchange and scrambling of hydrogen and deuterium do not occur, it is possible to elucidate the reduction mechanism with a reasonable degree of certainty by determining the deuterium distribution in the products. On the one hand, 1,6 addition (a)

(7) R. B. Bates, University of Arizona, personal communication, 1971.

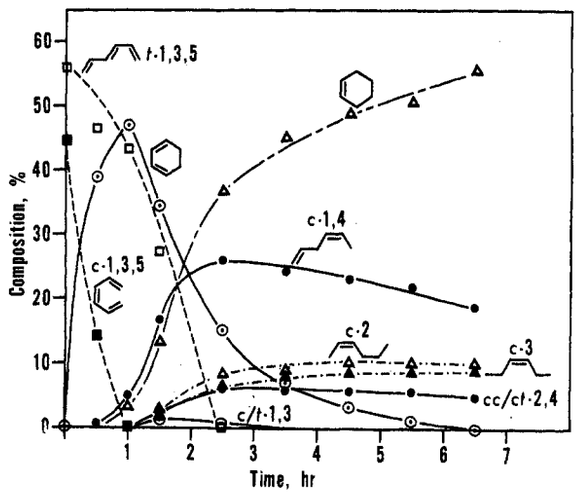
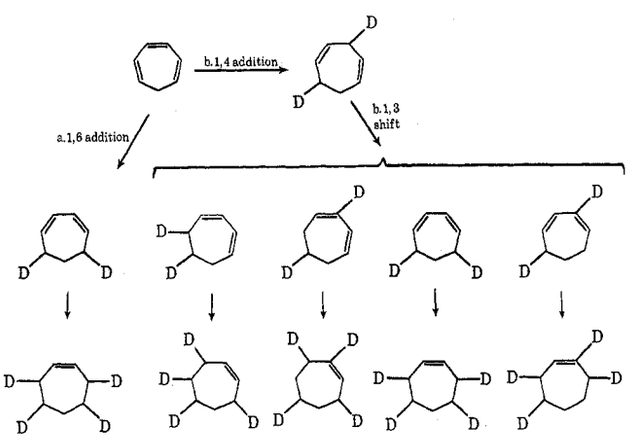


Figure 2.—Catalytic hydrogenation of *cis*- and *trans*-1,3,5-hexatriene (9.5 mmol) with methyl benzoate-$Cr(CO)_3$ (0.5 mmol) in *n*-pentane solution (50 ml) at 170° under 30 atm of H_2.

followed by 1,4 addition would yield 1,3-cycloheptadiene-d_2 with deuterium located all on the α-methylenes and cycloheptene-d_4 with deuterium distributed half on the α-methylenes and half on the β-methylenes (Scheme II). On the other hand, 1,4 addition followed

SCHEME II



by isomerization (b) would yield 1,3-cycloheptadiene-d_2 with deuterium located on the α- (50%) and β- (25%) methylenes and on the vinyl carbons (25%). It is assumed here that 1,4-cycloheptadiene-d_2 is formed as a reactive intermediate which undergoes rapid isomerization to 1,3-cycloheptadiene-d_2 by a 1,3 shift involving both hydrogen and deuterium in equal amounts. Further reduction of 1,3-cycloheptadiene-d_2 by 1,4 addition would yield cycloheptene-d_4 with deuterium located on the α- (50%) and β- (37.5%) methylenes and on the vinyl carbons (12.5%).

The deuterium distribution in the products determined by ^2H nmr is shown in Table I. The results are consistent with a mechanism involving reduction of 1,3,5-cycloheptatriene by 1,4 addition followed by isomerization (b). The direct 1,6-addition path (a) is ruled out by these results. These deuteration experiments have afforded a way of establishing the formation of an intermediate (1,4-cycloheptadiene) which is too reactive to be determined directly by standard techniques such as glc, uv, and ^1H nmr. The inter-

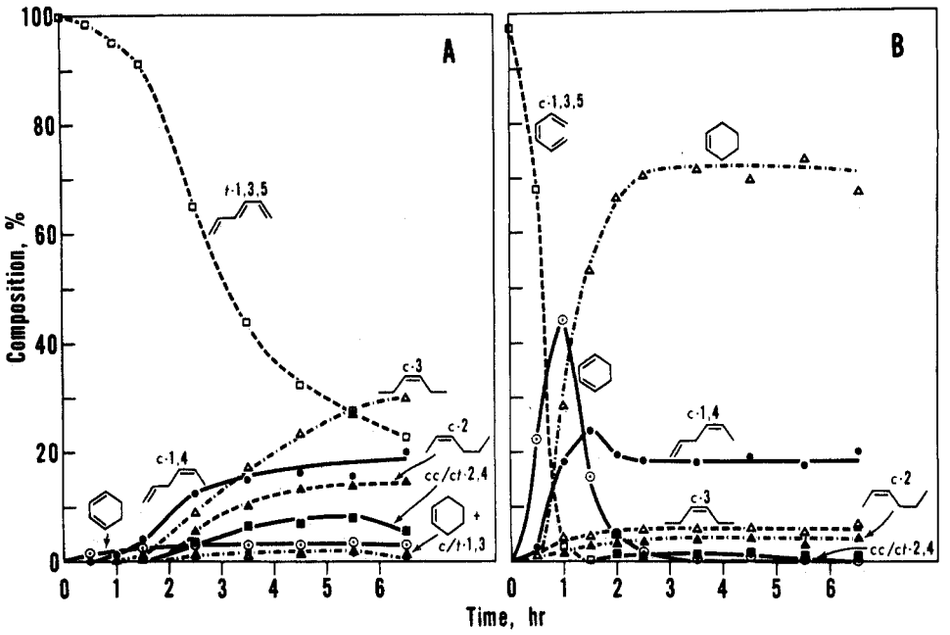


Figure 3.—Catalytic hydrogenation of (A) *trans*-1,3,5-hexatriene (1 mmol) and of (B) *cis*-1,3,5-hexatriene (1 mmol), with methyl benzoate–$Cr(CO)_3$ (0.05 mmol) in *n*-pentane solution (25 ml) at 160° under 30 atm of H_2.

TABLE I

DEUTERIUM DISTRIBUTION BY ^2H NMR

Deuterium in following positions[a]	—1,3-Cycloheptadiene-d_2,[b] %— After 2 hr	After 4 hr	—Calcd[c]— 1,6 Addn	1,4 Addn	—Cycloheptene-d_4,[b] %— After 4 hr	—Calcd[c]— 1,6 Addn	1,4 Addn
α-Methylene	40	45	100	50	50	50	50
β-Methylene	25	25		25	40	50	37.5
Vinyl carbon	35	30		25	10		12.5

[a] α-Methylene CDC=C, δ_{CDCl_3} 76–80 cps; β-methylene $CDCH_2C$=C, 80–84; vinyl CD=C, 22. [b] Fractions separated by preparative glc (run 2, Figure 1B). [c] See Scheme II, (a) 1,6 addition, (b) 1,4 addition followed by 1,3 shift.

mediate 1,4 dienes from noncyclic conjugated trienes are stable and their formation from methyl eleostearate has been established.[6] Further evidence of 1,4 diene formation from 1,3,5-hexatriene is reported below.

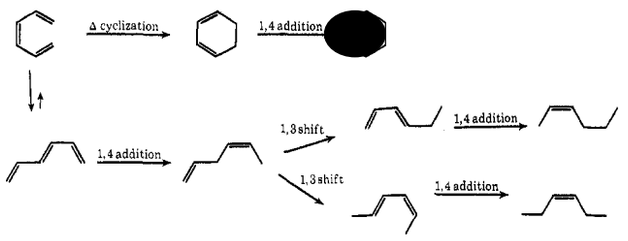
1,3,5-Hexatriene.—This simplest of acyclic conjugated trienes provided a suitable model. Rate studies with a mixture of *cis*- and *trans*-1,3,5-hexatriene showed the cis isomer to be more rapidly converted with methyl benzoate–$Cr(CO)_3$ than the trans isomer (Figure 2). 1,3-Cyclohexadiene and cyclohexene were important cyclic products. Acyclic products included *cis*-1,4-hexadiene, *cis,cis*- and *cis,trans*-2,4-hexadienes, and *cis*-2- and *cis*-3-hexenes. *cis*- and *trans*-1,3-hexadienes were also formed in minor amounts initially. 1,3-Cyclohexadiene is the product expected from cyclization of *cis*-1,3,5-hexatriene and *cis*-1,4-hexadiene, the product expected from 1,4 reduction of *trans*-1,3,5-hexatriene. 1,3-Cyclohexadiene is the valence tautomer of *cis*-1,3,5-hexatriene resulting from a Cope-type cyclization which is known to be a facile thermal reaction.[8] Control experiments demonstrated that this cyclization of *cis*-1,3,5-hexatriene occurs readily and irreversibly in the absence of catalyst. In a mixture of *cis*- and *trans*-1,3,5-hexatriene, complete conversion of the cis isomer to 1,3-cyclohexadiene occurred within 0.5–1 hr at 170° under either nitrogen or hydrogen pressure. Since the relative concentration of trans isomer remained unchanged, no cis → trans isomerization took place under these conditions. When pure 1,3-cyclohexadiene was heated under the same conditions, no ring opening was observed either.

To elucidate the reaction course further, *cis*- and *trans*-1,3,5-hexatriene were separated and purified by preparative glc and hydrogenated separately. Hydrogenation of pure *trans*-1,3,5-hexatriene proceeded as expected by 1,4 addition and yielded predominantly *cis*-1,4-hexadiene as the most important intermediate (Figure 3A). Other dienes included in decreasing concentration 2,4-hexadiene, 1,3-cyclohexadiene, and 1,3-hexadienes. The monoenes were composed of *cis*-3- and *cis*-2-hexenes, together with minor amounts of cyclohexene. Since cyclohexadiene would be derived from cyclization of *cis*-1,3,5-hexatriene, this evidence indicates that a trans → cis isomerization of hexatriene occurs to a small, but significant, degree. Hydrogenation of *cis*-1,3,5-hexatriene (97% pure) resulted in cyclization as the main reaction (Figure 3B). 1,3-Cyclohexadiene reached a maximum of 45% within 1 hr and was rapidly converted to cyclohexene, which leveled off at 70–73%. Cyclization was accompanied by 1,4 reduction as evidenced by the formation of *cis*-1,4-hexadiene, which peaked at 25% and leveled off at 18%. The corresponding conjugation and reduction products were observed (2,4-hexadiene, 2- and 3-hexenes).

These results clearly support the reaction sequence in Scheme III. On the one hand, cyclization of *cis*-1,3,5-hexatriene is followed by 1,4 reduction of 1,3-cyclohexadiene. On the other hand, hydrogenation of *trans*-1,3,5-hexatriene by 1,4 addition is followed by isomerization of *cis*-1,4-hexadiene to a mixture of 1,3- and 2,4-hexadienes, which are in turn reduced to *cis*-2- and *cis*-3-hexenes, respectively. There is also clear evidence for an equilibration between *trans*- and *cis*-1,3,5-hexatrienes that favors the trans isomer.

(8) (a) K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964); (b) D. S. Glass, J. W. H. Watthey, and S. Winstein, *Tetrahedron Lett.*, 377 (1965); (c) E. N. Marvell, G. Caple, and B. Schatz, *ibid.*, 385 (1965); (d) E. Vogel, W. Grimme, and E. Dinne, *ibid.*, 391 (1965).

SCHEME III



Evidence for this type of geometric isomerization has already been observed with α- and β-eleostearate.[6] Equilibrium K (trans/cis) values of 3.97 (0°) and 2.97 (5°) were reported[9] for the iodine-catalyzed isomerization of 1,3,5-hexatriene. We have also reported on the reduction by 1,4 addition of 1,3-cyclohexadiene and 1,4-hexadiene[4c] and on the isomerization of 1,4 dienes[5b,10] catalyzed by $Cr(CO)_3$ complexes. The mechanisms advanced involve a diene–$H_2Cr(CO)_3$ intermediate in the 1,4 addition, and allyl–$HCr(CO)_3$ or pentadienyl–$HCr(CO)_3$ intermediates in the isomerizations by 1,3-hydrogen shift. The catalytic isomerization of *trans*-1,4-hexadiene occurred much more readily than that of *cis*-1,4-hexadiene, and steric hindrance was invoked in the pentadienyl hydride intermediate from the cis isomer.[10] The same steric hindrance in the hydride complex from the *cis*-1,4-hexadiene intermediate would account for its slow rate of hydrogenation and the slow conversion of its precursor, *trans*-1,3,5-hexatriene.

Experimental Section

Materials.—The catalyst methyl benzoate–$Cr(CO)_3$ was purchased (Strem Chemicals, Inc.).[11] Cycloheptatriene (Chemical Samples Co.) was distilled and chromatographed through a short alumina column. It was 98% pure by glc on a 1,2,3-tris(2-cyanoethoxy)propane (TCEP) column. An unidentified impurity (2%) was inert under hydrogenation conditions. 1,3,5-Hexatriene (Aldrich Chemical Co., K & K Laboratories, Inc.) was pure by glc and consisted of 56–64% trans and 36–44% cis isomers (TCEP column). Isomer identification was based on glc after reaction with iodine and maleic anhydride.[12] The cis and trans isomers were separated by preparative glc on a β,β′-oxydipropionitrile (ODPN) column (14 ft × 0.25 in.; 20% on Chromosorb W, 60–80 mesh). The trans fraction, which emerged first, was pure (by glc on an ODPN column). The cis fraction (97%) contained 3% trans isomer. Other hydrocarbons of high-purity grade used for identification were purchased (Chemical Samples Co.).

Hydrogenation and Separation.—The hydrogenation and deuteration procedures were the same as before.[4c,5] Products from from cycloheptatriene deuteration were first distilled and then separated by preparative glc on a Carbowax 20M column (8 ft × 0.25 in.; Chromosorb W, 60–80 mesh; 20% liquid phase). Control runs were made to check the thermal valence isomerization of *cis*-1,3,5-hexatriene. A 44:56% mixture of *cis*- and *trans*-1,3,5-hexatriene (1 g) in *n*-pentane (50 ml) was heated in a 150-ml autoclave at 170° in the absence of catalyst. In one run under hydrogen pressure (200 psi), the cis isomer was completely converted to 1,3-cyclohexadiene during a heat up of 30 min and the trans isomer was left unchanged. In another run under nitrogen pressure (50 psi), this conversion occurred within 1 hr after the temperature of the reaction mixture was reached. When pure 1,3-cyclohexadiene was heated under the same conditions, no formation of *cis*-1,3,5-hexatriene was observed within 6 hr.

Analyses.—Analyses and product identification were carried out by glc on three different columns (TCEP, ODPN, and Carbowax 20M) as before.[4c] The uv spectrum (cyclohexane) of a fraction distilled from partially hydrogenated cycloheptatriene (glc analysis: 26.5% cycloheptatriene, 70.8% cycloheptadiene, and 2.7% cycloheptene) showed a maximum at 247.5 nm (ε 6125) due to 1,3-cycloheptadiene [lit.[13] λ_{max} 248 nm (ε 7150)] and a shoulder at 265 nm due to unreacted 1,3,5-cycloheptatriene.

Mass spectral analyses of deuterated products were done on a Nuclide 12-90-DF mass spectrometer at 70 eV with a 150° metal inlet. Deuterium analyses were calculated as atoms per molecule in excess of natural abundance. The mass spectrum of 1,3,5-cycloheptatriene obtained by preparative glc (Carbowax 20M column) after partial reduction with D_2 (Figure 1B, 2 hr) was the same in the parent peak region as that of the starting material. It contained, therefore, no deuterium (cycloheptatriene-d_0). 1,3-Cycloheptadiene was separated by preparative glc from deuteration mixtures after 2 hr and 4 hr and cycloheptene was separated after 4 hr (Figure 1B). Fractions of deuterated 1,3-cycloheptadiene had an M peak of 96 corresponding to cycloheptadiene-d_2. Relative isotopic peaks, d_0, d_1, d_2, and d_3 were of the same order of intensity or below the corresponding peaks M − 2, M − 1, M, and M + 1 in a nondeuterated 1,3-cycloheptadiene standard. The deuterated cycloheptene fraction had an M peak of 100 corresponding to cycloheptene-d_4. Relative isotopic distribution d_3, d_4, and d_5 was of the same order of magnitude as the distribution M − 1, M, and M + 1 in nondeuterated cycloheptene.

^1H nmr spectra ($CDCl_3$, 100 MHz, in τ values relative to tetramethylsilane) showed the following resonances in 1,3-cycloheptadiene fractions: τ 8.16 (β-methylene, 2 H), 7.72 (α-methylene, 4 H), 4.34 (vinyl, 4 H) [1,4-cycloheptadiene reference:[14] τ 7.82 (α-methylene, 4 H), 7.20 (α,α-methylene), 4.35 (vinyl 4 H)]. ^2H nmr spectra ($CDCl_3$, 15.4 MHz in cycles per second relative to $CDCl_3$) showed three resonances: in 1,3-cycloheptadiene-d_2 fractions, δ 83.6 (D on β-methylene, $CDCH_2$-C=C), 75.8 (D on α-methylene CDC=C), and 22.3 (D on vinyl carbon, –CD=C–); in cyclohexene-d_4, δ 88.1 (D on β-methylene), 79.6 (D on α-methylene), and 22.1 (D on vinyl carbon). Relative magnitude of these deuterium resonances are reported in Table I.

Registry No.—1,3,5-Cycloheptatriene, 544-25-2; *cis*-1,3,5-hexatriene, 2612-46-6; *trans*-1,3,5-hexatriene, 821-07-8.

Acknowledgment.—The author is grateful to Professor R. B. Bates, University of Arizona, for the reference 1,3- and 1,4-cycloheptadienes[14] and for helpful discussions; to W. K. Rohwedder for mass spectral analyses; and to C. A. Glass for nmr analyses.

(9) C. W. Spangler, *J. Org. Chem.*, **31**, 346 (1966).

(10) E. N. Frankel, *J. Catal.*, **24**, 358 (1972).

(11) The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

(12) C. W. Spangler and G. F. Woods, *J. Org. Chem.*, **30**, 2218 (1965).

(13) A. P. TerBorg and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **80**, 1229 (1961).

(14) R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **91**, 4608 (1969), especially footnote 9.