cyclohexene into the corresponding alcohols. Although our original experiments required oxidation to the ketones for analysis, it proved possible to resolve the alcohols on a 150-foot diglycerol capillary column at 54°; 18% cis-2-, 30% trans-2-, 27% cis-3-, and 25% trans-3-methylcyclohexanol.

An identical procedure applied to 1.10 g. (10 mmoles) of 3,3-dimethylcyclohexene revealed the presence of 40% of 2,2-dimethylcyclohexanol and 60% of 3,3-dimethylcyclohexanol (Ucon polar column).

[Contribution from the Denver Research Center of The Ohio Oil Co. Littleton, Colo.]

The Cyclic Trimerization of Acetylenes Over a Ziegler Catalyst

By Eugene F. Lutz

Acetylene and six substituted acetylenes have been trimerized successfully over a Ziegler catalyst to benzene and substituted benzenes in good yields. The evidence obtained here shows that the polymerization of acetylenes proceeds by a mechanism different from that generally accepted for the polymerization of α-olefins in this catalyst system.

Introduction and Results

Although considerable effort has been devoted to the study of the polymerization of α-olefins over Ziegler catalysts,[1] very little has been published concerning the polymerization of acetylenes over these highly reactive and selective complexes. Three publications, one a patent, by Giulio Natta and co-workers,[2] describe the formation of high molecular weight polymers from acetylene,[2ab] phenylacetylene,[2a] 1-butyne[2a] and 1-hexyne[2c] over AlR$_3$–TiX$_4$ organometallic complex catalysts. Natta presents evidence indicating that the polymers formed are long chains of alternating single and double bonds.

More recently Franzus, et al.,[3] have shown that disubstituted acetylenes can be trimerized to hexasubstituted benzenes by regulating the ratio of (i-Bu)$_3$Al to TiCl$_4$ in the organometallic catalyst. These results are similar to those reported by Zeiss and co-workers[4] in the cyclic trimerization of internal acetylenes over organochromium[5] catalysts.

The literature to date suggests that monoalkylacetylenes are far too reactive to undergo cyclic trimerization and instead react very rapidly to form high molecular weight polymers. We have found, however, that in spite of their high reactivity, acetylene and monoalkylacetylenes can be trimerized over a Ziegler-type catalyst to benzene and trialkylbenzenes, respectively, by use of high

dilution techniques, i.e., a large volume of solvent, small catalyst particle size, efficient stirring and low reactant concentration.

$$3R-C\equiv C-R' \xrightarrow{\text{AlEt}_3\text{-TiCl}_4}$$

Ia, R = H; R' = H
Ib, R = alkyl, R' = H
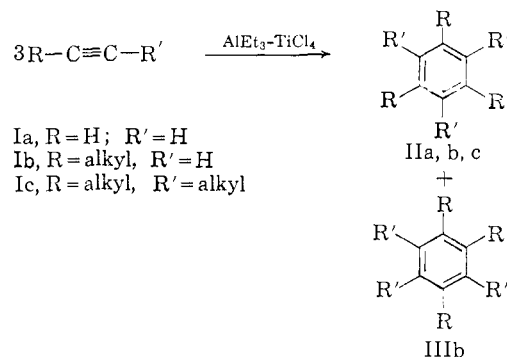Ic, R = alkyl, R' = alkyl

IIa, b, c

+

IIIb

Table I lists the acetylenes that have been trimerized to aromatic hydrocarbons in this Laboratory. This technique offers a convenient method for synthesizing substituted benzenes not readily available by other methods or from other sources.

Table I

ACETYLENES USED AND PRODUCTS OBTAINED

Substitution	Reacn. temp., °C.	Trimer	Yield, %	High polymer, %[c]
None	23–30[a],[b]	Benzene	49.1	24.1
Methyl	23–36[a]	Mesitylene	40.4	9.3
		Pseudocumene	21.1	
Ethyl	23–30[a]	1,3,5-Triethylbenzene	35.5	7.3
		1,2,4-Triethylbenzene	17.0	
Butyl	24–32[a]	1,3,5-Tributylbenzene	59.8	..
Dimethyl	23–34[a]	Hexamethylbenzene	80.2	2.2[d]
Diethyl	24–32[a]	Hexaethylbenzene	76.5	..
Dibutyl	~86	Hexabutylbenzene[f]	52.2[e]	4.6[d]

[a] Reactions were exothermic, producing an 11–16° rise in temperature. [b] The temperature gradually dropped toward the end of the reaction, indicating a loss of catalyst activity. [c] Estimated by subtracting the weight of the organometallic catalyst from the total weight of the solids obtained from reaction; see Experimental for details. [d] Because of the reaction workup used, this represents the upper limit of high polymer formation; see the Experimental for further discussion. [e] A small amount of another product, perhaps a dimer, also was obtained. [f] This appears to be the first synthesis of this compound.

(1) See G. Natta and I. Pasquon in D. D. Eley, P. W. Selwood and Paul B. Weisz, "Advances in Catalysis and Related Subjects," Academic Press, Inc., New York, N. Y., 1959, Vol. XI, pp. 1–66, for review and leading references.

(2) (a) G. Natta, P. Pino and G. Mazzanti, Italian Patent 530,753, July 15, 1955 (C. A., **52**, 15128b (1958)); (b) G. Natta, G. Mazzanti and P. Corradini, Atti Accad. nazl. Lincei Rend. Classe sci. fiz. mat. e nat., **25**, 3 (1958) (C. A., **53**, 13085i (1959)); (c) G. Natta, G. Mazzanti, G. Pregaglia and M. Peraldo, Gazz. chim. ital., **89**, 465 (1959) (C. A., **54**, 11967i (1960)).

(3) B. Franzus, P. J. Canterion and R. A. Wickliffe, J. Am. Chem. Soc., **81**, 1514 (1959).

(4) H. Zeiss in "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 411–421.

(5) G. Wilke and M. Kroner, Angew. Chem., **71**, 574 (1959), obtained a bis-(hexamethylbenzene)-chromium complex from the reaction of 2-butyne over a Ziegler catalyst prepared from AlEt$_3$ and CrO$_2$Cl$_2$.

Discussion

Natta and co-workers have shown that, when AlR_3–$TiCl_3$ catalysts are used in which either radioactively labeled alkyl groups or phenyl groups are incorporated into the catalyst complex, the labeled parts of the catalyst appear in the polymer resulting from α-olefin polymerization.[6,7] This has been interpreted as evidence for an anionic polymerization mechanism initiated by rupture of a C–Al bond in the catalyst.[8]

Although the high polymers obtained here could not be analyzed for ethyl group incorporation, it is clear that the major part, if not all, of the polymerization took place without rupture of the C–Al bonds of the catalyst. Had metal–alkyl bond rupture occurred in a manner similar to that proposed for α-olefin polymerization,[8] cyclization to benzene or alkylated benzenes would be an extremely unlikely possibility and, if it did occur, ethyl substituted benzenes would be the expected products. Further, in the case of the dialkylacetylenes, a C–C bond would have to be broken in their cyclization to hexaalkylbenzenes and this would be completely unexpected under the mild reaction conditions used.

In the light of the above discussion, it seems that the trimerization of acetylenes over an $AlEt_3$–$TiCl_4$ complex catalyst must proceed by means of surface catalysis and, therefore, appears to be a truly catalytic process.[9] The acetylene is probably chemisorbed in the first step of the reaction to produce a polarized intermediate which can interact with its polarized neighbors to yield either trimer or high polymer as shown:

$2RC{\equiv}CR'$
R = H, alkyl
R'= H, alkyl
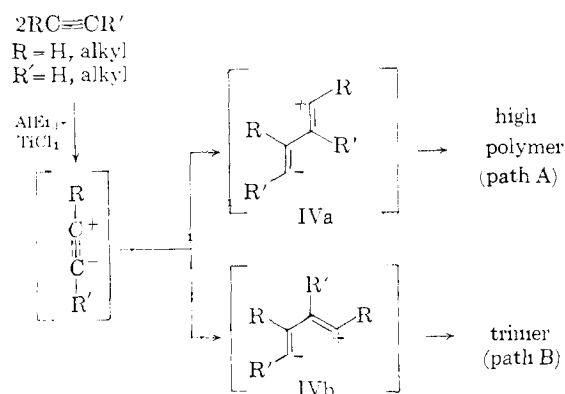
The ease with which this reaction occurs may be due to the acetylene's two π-orbitals, one of which can bond to the catalyst surface leaving the other available for reaction with other activated molecules chemisorbed on the catalyst surface.

The very selective trimerization of 2-butyne, 3-hexyne and 5-decyne to hexasubstituted benzenes, almost exclusively, illustrates the importance of steric factors in this surface reaction. As can be seen from the proposed mechanism above (but more clearly from molecular models), where two alkyl groups are attached to the triple bond, con-

siderable steric hindrance would be encountered in forming intermediate IVa. However, assuming intermediate IVa is formed, attack on the active end of the growing chain is completely blocked by alkyl groups. This accounts for the ease with which dialkylacetylenes undergo cyclic trimerization to the exclusion of straight chain polymerization.

In the case of the monoalkylacetylenes, the steric control of the reaction is demonstrated in a slightly different way. Here the possibility of forming more than one trimeric isomer exists and, as the bulk of the alkyl substituent increases, the formation of the symmetrically substituted isomer predominates. Thus, mesitylene accounts for 65.7% of the methylated benzenes formed while 1,3,5-tributylbenzene is the only butylated benzene obtained.

Although the catalyst gives a slightly acid solution when hydrolyzed in water, comparison of the results obtained here with those obtained for the Lewis acid-catalyzed trimerization of acetylenes is completely different. For example, when methylacetylene is passed over a strong acid catalyst (85% silica–15% alumina catalyst impregnated with chromium trioxide[10]) at $90°$, a 56.4% yield of pseudocumene and a 10.2% yield of mesitylene is obtained.[11] The ratio of mesitylene to pseudocumene is 0.18, while in our work the ratio is 1.9. In addition, an attempt to trimerize 2-pentyne over the silica–alumina catalyst failed,[11] whereas 2-butyne, 3-hexyne and 5-decyne trimerize readily over a Ziegler catalyst. These data suggest that the $AlEt_3$–$TiCl_4$ organometallic complex catalyst may not behave as an acid in n-heptane. Additional work is planned which may help to resolve this problem.

Acknowledgment.—The author wishes to express his appreciation to Mr. Harold Pinkham for experimental help.

Experimental[12]

Catalyst Preparation. General Procedure.[13]—To a stirred solution of 3.4 g. (0.03 mole) of aluminum triethyl in about 200 cc. of pure,[14] dry n-heptane was added 1.9 g. (0.01 mole) of titanium tetrachloride in about 5 cc. of n-heptane. The black, insoluble organometallic complex immediately precipitated. The catalyst solution then was stirred for 3 min. in a high speed homogenizer to ensure complete reaction and to reduce the particle size of the catalyst. The catalyst solution was poured into a 1-liter 3-necked Morton flask, stoppered and removed from the glovebox. Under a stream of prepurified nitrogen the 3-necked Morton flask was equipped for reaction and an additional 400 cc. of pure, dry n-heptane was added.

Benzene.—Acetylene was passed at a rate of about 30 cc./min. into the catalyst solution with vigorous stirring over a period of 4.5 hours. The reaction temperature

(6) Reference 1, p. 32 and following.

(7) G. Natta and G. Mazzanti, *Tetrahedron*, **8**, 95 (1960).

(8) Reference 1, p. 9.

(9) Natta has shown that polymerization of α-olefins over $AlEt_3$–$TiCl_3$ is catalytic only in $TiCl_3$; ref. 1, p. 45.

(10) This catalyst would be about as strongly acid as 90% sulfuric acid; H. A. Benesi, *J. Am. Chem. Soc.*, **78**, 5490 (1956).

(11) A. Clark, J. P. Hogan, D. R. Witt and W. C. Lanning, Proc. Fifth World Petroleum Congress, New York, N. Y., June, 1959, Sec. IV, p. 267.

(12) All melting and boiling points are uncorrected. Barometric pressure is usually about 620 mm. All of the substituted acetylenes were purchased from Farchan Research Laboratories, Wickliffe, Ohio.

(13) All of the operations were carried out in a glove-box, purged with Matheson prepurified nitrogen.

(14) The infrared spectrum of commercial n-heptane showed an extraneous band when compared with the API spectrum of pure n-heptane. This impurity could be removed by shaking n-heptane with activated alumina.

gradually rose from 22.5 to 39° in about 2 hours, and then began to decrease slowly. When the temperature had dropped to between 30 and 35°, the reaction was terminated. Twenty-three grams of acetylene had been added as determined by the weight loss of the acetylene cylinder. After standing overnight, the reaction solution was centrifuged to separate the black precipitate from the remainder of the solution. The black solid weighed 8.08 g. after being dried in a vacuum desiccator. The percentage of benzene in n-heptane was determined by gas–liquid chromatography (g.l.c.) using 2 m. of Perkin–Elmer K column at room temperature. Calculation showed that 11.295 g. (49.1% yield) of benzene was formed. The benzene was identified by comparison of its g.l.c. retention time with that of a sample of reagent grade benzene and by preparation of its 1,3-dinitro derivative, m.p. 86–87°. The reported[15] m.p. is 89.6°. The n-heptane solution then was evaporated to dryness, leaving a brownish-yellow powder, which weighed 3.08 g. after being dried in a vacuum desiccator. Total weight of all solids obtained was 11.16 g. Subtracting the expected weight of the spent catalyst[16] from this places the weight of high polymer formed at 5.55 g. (24.1% yield).

Mesitylene and Pseudocumene.—Over a period of 2.5 hours, 25.873 g. of methylacetylene[12] was added to the catalyst solution as described above, causing the reaction temperature to rise from 23 to 36°. The reaction solution was worked up as before and 4.20 g. of black solid was obtained after drying. The n-heptane solution was distilled at first through a short, glass-helices packed column and later, as the solvent decreased, through a 5.5-inch vacuum jacketed Vigreux column. After the n-heptane was removed, 11.22 g. of a mixture of mesitylene and pseudocumene distilled at 148°, n^{23}D 1.4985 (lit. n^{20}D 1.4967 for mesitylene[17] and n^{20}D 1.5044 for pseudocumene[18]). An additional 4.99 g. of this mixture containing a small amount of n-heptane was also obtained. The total weight of solids that precipitated out of the n-heptane solution as it was distilled amounted to 3.81 g. The total solid obtained from the reaction mixture was 8.01 g. and, when the expected weight of spent catalyst[16] was subtracted, the estimated weight of high polymer formed was 2.40 g. (9.3% yield).

G.l.c. analysis (4 m. of Perkin–Elmer K column was used at 80°) showed that 15.91 g. of the total liquid collected during distillation was aromatic hydrocarbon. This is a yield of 61.5%, of which mesitylene accounts for 40.4% and pseudocumene for 21.1%. The g.l.c. retention times of mesitylene and pseudocumene were compared with those of authentic samples.

1,3,5- and 1,2,4-Triethylbenzene.—Over a period of 4 hours, 16.5 g. of 1-butyne[12] was added to the catalyst solution as described for the benzene synthesis above, causing the reaction temperature to rise from 23 to 30°. The reaction solution was worked up as previously described and 3.1 g. of dry catalyst was obtained. After the n-heptane solvent was removed, distillation of the reaction solution was continued under vacuum, giving 8.7 g. of a liquid boiling at 99–102° (20 mm.), $n^{19.5}$D 1.4896 (lit.[19] for 1,3,5-triethylbenzene: b.p. 215.92° (760 mm.), n^{20}D 1.4958). The pot residue amounted to 3.7 g. The pot residue plus the catalyst previously recovered amounted to 6.8 g. and, when the expected weight of spent catalyst[16] was subtracted, the estimated weight of high polymer formed was 1.2 g. (7.3% yield).

G.l.c. analysis (4 m. of Perkin–Elmer K column was used at 110°) showed that the liquid fraction from above

(15) F. McCamish and A. Salathe, *J. Am. Chem. Soc.*, **50**, 1785 (1928).

(16) An experiment was carried out in which the Ziegler catalyst was prepared as usual except that it was not used for reaction. Instead, the black precipitate was separated and dried (wt. 3.34 g.) and the n-heptane solution was evaporated to dryness, giving 2.27 g. of a white powder. The total solid thus obtained weighed 5.61 g. This was considered to be the expected weight of the spent catalyst and was subtracted from the total solid obtained in each of the experiments above to get an estimate of the amount of high polymer formed in each case. Hydrolysis of both the green-black solid (color when dry) and the white solid gave slightly acid solutions ($pH \sim 5$.)

(17) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Oxford Univ. Press, New York, N. Y., 1953, Vol. III, p. 272.

(18) I. Heilbron and H. M. Bunbury, *ibid.*, Vol. I, p. 618.

(19) L. C. Gibbons, J. F. Thompson, T. W. Reynolds, J. I. Wright, H. H. Chanan, J. M. Lamberti, H. F. Hipsher and J. V. Karabinos, *J. Am. Chem. Soc.*, **68**, 1131 (1946).

consisted of two compounds which had retention times of 20.0 and 23.6 minutes, respectively. By analogy with the known trimethylbenzenes it was concluded that the symmetrical isomer should have the shorter retention time and therefore the first peak was assigned to 1,3,5-triethylbenzene. Determination of the peak areas with a planimeter placed the yield of 1,3,5-triethylbenzene at 35.5% and that of 1,2,4-triethylbenzene at 17.0%. 1,3,5-Triethylbenzene accounted for 67.3% of the two triethylbenzenes formed. The infrared spectrum of the liquid product had all the bands characteristic of aromatic hydrocarbons.

1,3,5-Tributylbenzene.—To a stirred catalyst solution was added 25.6 g. (0.3 mole) of 1-hexyne[12] in 60 cc. of dry n-heptane over a period of 160 min. During this period the reaction temperature rose from 24 to 32° The reaction solution was centrifuged and the recovered black catalyst weighed 3.5 g. after drying. The n-heptane solution was distilled, giving 20.8 g. of a liquid product boiling at 94–107° (0.5 mm.). The pot residue was a thick sirup and weighed 6.3 g. Redistillation of the liquid product gave 15.3 g. boiling at 99–100° (0.2 mm.), $n^{20.5}$D 1.4868 (lit.[20] for 1,3,5-tributylbenzene: b.p. 315°, n^{20}D 1.4870). The infrared spectrum of the compound showed bands at 3000 (m, shoulder), 1775(w), 1613(s), 1510(m) and 1467(vs) cm.$^{-1}$, all characteristic of an aromatic hydrocarbon.[21]

G.l.c. analysis (2 m. of Perkin–Elmer K column was used at 200°) of the product gave only one peak at 4.9 minutes and thus it was concluded that 1,3,5-tributylbenzene was the only tributylbenzene found.

The theoretical yield of 1,3,5-tributylbenzene was 59.8%.

Hexamethylbenzene.—To a stirred catalyst solution was added 16.33 g. (0.3 mole) of 2-butyne[12] in 60 cc. of dry n-heptane over a period of about 2 hours. The reaction temperature rose from 23 to 34° in this interval. After the reaction solution was centrifuged to remove the black precipitate, the n-heptane solution was evaporated to dryness. The resulting white solid was washed several times with ether and the ether solution was evaporated to dryness. Finally, both the black solid and the white solid that remained were placed together and washed with ether 3 or 4 times, after which the ether solution was evaporated to dryness. A total of 13.10 g. (80.2% yield) of crude hexamethylbenzene (m.p. 155–60°) was thus obtained, leaving 5.97 g. of spent catalyst. The difference between the spent catalyst obtained here and that expected[16] amounted to only 0.36 g. This difference could be due either to high polymer formation or else to incomplete extraction of the hexamethylbenzene. Thus, the 2.2% yield of polymer shown in Table I would be the upper limit of polymer formation.

The hexamethylbenzene was identified by its m.p., 162–163° (after one recrystallization from absolute alcohol), its identity with the infrared spectrum of pure hexamethylbenzene,[22] and its orange-colored picrate which melted at 169.5–170.5°. The reported m.p. for hexamethylbenzene[23] is 164° and for the picrate[24] is 170° (O-Y plates).

Hexaethylbenzene.—To a stirred catalyst solution was added 24.6 g. (0.3 mole) of 3-hexyne[12] in 60 cc. of dry n-heptane over a period of 2.5 hours. The reaction temperature rose from 24 to 32°. The solution then was heated at about 43° overnight to ensure complete reaction. The reaction workup was the same as described for hexamethylbenzene. Thus, 25.3 g. of crude hexaethylbenzene was obtained which, after one recrystallization from 95% alcohol, weighed 18.8 g. (76.5% yield) and melted at 126–128° (lit.[25] m.p. 129°). Its infrared spectrum matched that of hexaethylbenzene published by Richards and Thompson.[26]

(20) D. A. McCaulay, A. P. Lien and P. J. Launer, *ibid.*, **76**, 2354 (1954).

(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1958, pp. 64–91.

(22) "Documentation of Molecular Spectroscopy," Butterworths Scientific Publications, London, and Verlag Chemie, Weinheim/ Bergstr., 1956, Spectral Card for Hexamethylbenzene.

(23) I. Heilbron and H. M. Bunbury, ref. 17, Vol. II, p. 670.

(24) O. L. Baril and E. S. Hauber, *J. Am. Chem. Soc.*, **53**, 1087 (1931).

(25) I. Heilbron and H. M. Bunbury, ref. 17, Vol. II, p. 657.

(26) R. E. Richards and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A195**, 4 (1948–1949).

Hexabutylbenzene.—To a stirred catalyst solution, maintained at about 86°, was added 41.4 g. (0.3 mole) of 5-decyne[12] in 60 cc. of dry n-heptane over a period of about 2 hours. The stirred solution was refluxed gently overnight. After cooling, the reaction solution was centrifuged and then the n-heptane solvent was distilled, leaving a brown liquid which solidified on cooling. No 5-decyne was recovered from the distillation. The brown solid obtained weighed 38.3 g. and appeared to be wet with an oil. After several recrystallizations from 95% alcohol it was possible to concentrate the oil (it was insoluble in the alcohol) by decanting the hot alcohol solution away from it. This oil, as yet unidentified, was distilled at 100–112° (0.7 mm.), $n^{21.5}_D$ 1.4670, and amounted to 2.9 g. The recrystallized hexabutylbenzene weighed 21.6 g. (52.2% yield) and had a melting point of 56.5–57.5°.

Anal.[27] Calcd. for $C_{30}H_{54}$: C, 86.88; H, 13.12. Found: C, 86.90; H, 13.07.

(27) The analysis was performed by Huffman Microanalytical Laboratories, Wheatridge, Colo.

The molecular weight was determined by the Beckmann method and found to be 405 while that calculated for hexabutylbenzene is 414.8. The infrared spectrum (determined in KBr disk) of hexabutylbenzene was compared with that of hexaethylbenzene in the region between 1650 and 1450 cm.$^{-1}$, characteristic of the skeletal stretching modes of carbon–carbon bonds in aromatic compounds,[28] and found to match very closely. Thus, hexabutylbenzene had bands at 1638 (w, broad), 1500(m), 1472(s) and 1455(m) cm.$^{-1}$ while hexaethylbenzene had bands at 1640(w, broad), 1503(m), 1475(m-s) and 1461(s) cm.$^{-1}$. The band at about 1638 cm.$^{-1}$ (w, broad) was also present in the spectrum of hexamethylbenzene.

The recovered catalyst weighed 7.5 g. after being dried in a vacuum desiccator. The difference between this weight and that of the expected weight of spent catalyst[16] was 1.9 g. This difference could be due either to high polymer formation or else to incomplete washing of the recovered catalyst.

(28) L. J. Bellamy, ref. 21, p. 69.

The Addition of Deuterium Bromide to 1,3-Cyclohexadiene

BY GEORGE S. HAMMOND[1] AND JOHN WARKENTIN

RECEIVED NOVEMBER 22, 1960

The addition of deuterium bromide to 1,3-cyclohexadiene in pentane solution gives a mixture of products which probably include both *cis* and *trans* isomers of the 1,2- and 1,4-adducts; *cis* products predominate over *trans* products and the total 1,4-adduct exceeds the total 1,2-adduct by a small amount. Although the results are not compelling, they suggest that addition occurs by a 1,4-*cis* process and a 1,2-*trans* process and that some jumbling of products occurs by stereospecific allylic rearrangements.

The polar addition of hydrogen bromide to 1,2-dimethylcyclohexene[2] and of hydrogen chloride to 1,2-dimethylcyclopentene[3] have been shown to proceed by a stereospecific, *trans* process. The present study was undertaken to determine the steric course of addition to a conjugated diene. The substrate chosen for the study was 1,3-cyclohexadiene and the addend was deuterium bromide.

Results and Discussion

Four addition products can conceivably be formed in the addition reaction as is shown by the equation
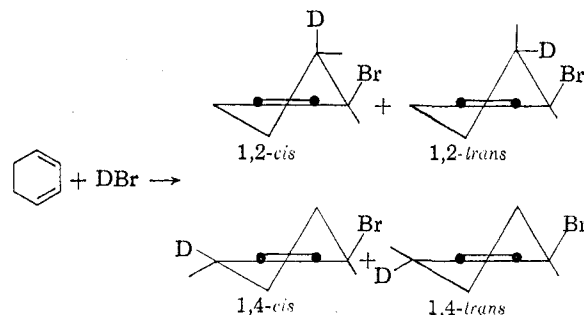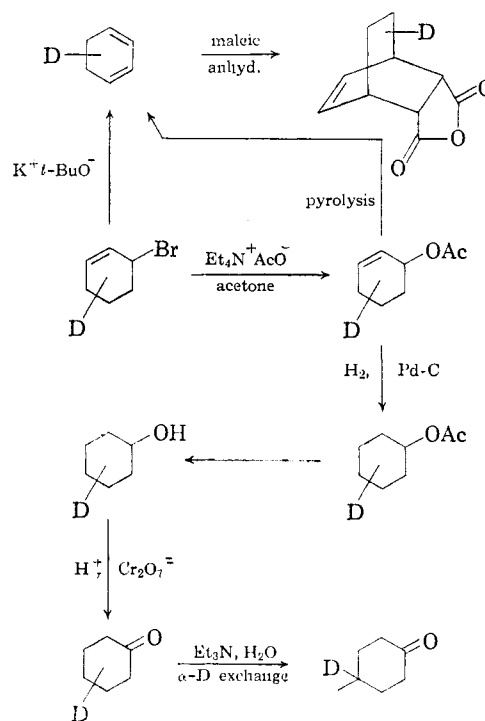

The deuteriobromocyclohexene was partially analyzed by the scheme

(1) Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, Calif.

(2) G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, **76**, 4121 (1954).

(3) G. S. Hammond and C. H. Collins, *ibid.*, **83**, in press (1961).

Results of the degradative experiments are gathered in Table I and show that the reaction must have taken more than one course. Both elimination sequences remove 12.5% of the deuterium. This implies that the original product contained only 12.5% of the 1,2-*trans*-adduct. The