separated. This was crystallized from dilute ethanol, m.p. 107–109°.

Anal. Calcd. for $C_{26}H_{30}O_4N_2S$: C, 67.0; H, 6.4; N, 6.0; S, 6.8. Found: C, 67.6; H, 7.0; N, 5.6; S, 6.3.

Methyl 4,6-diphenoxyhexanoate. A solution of 40.8 g. of 4,6-diphenoxyhexanoic acid in 60 ml. of absolute methanol was saturated with dry hydrochloric acid. The reaction mixture was allowed to stand at room temperature for 24 hr. and methanol was removed *in vacuo*. The residue was extracted with ether which was washed with 3% sodium bicarbonate solution to remove unchanged acid and then dried over anhydrous sodium sulfate. After the remotion of the solvent, the residue was distilled under reduced pressure giving 39 g. (91.3%) of the ester collected at 203–205°/1 mm.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.1; H, 7.0. Found: C, 72.1; H, 6.8.

4,6-Diphenoxyhexanol. To a stirred suspension of 9.0 g. of lithium aluminium hydride in 115 ml. of anhydrous tetrahydrofuran, cooled in an ice-salt bath, was added dropwise a solution of 39.0 g. of methyl 4,6-diphenoxyhexanoate in 150 ml. of anhydrous tetrahydrofuran. The reaction mixture was worked up as described for preparation of 2,4-diphenoxybutanol. The yield of product, b.p. 215°/1 mm., was 32.9 g. (88%).

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.6; H, 7.7. Found: C, 76.0; H, 8.2.

1-Bromo-4,6-diphenoxyhexane. Phosphorus tribromide, 11.6 g., was treated with 30.5 g. of 4,6-diphenoxyhexanol by the procedure described for the preparation of 1-bromo-2,4-diphenoxybutane. Distillation of the residue gave 30.6 g. (82%) of a liquid boiling at 197–200°/1 mm.

No further attempt was made at purification but this product was used at once for the next preparation.

6,8-Diphenoxyoctanoic acid. (a). *From 1-bromo-4,6-diphenoxyhexane.* The general procedure used was that described for the preparation of 4,6-diphenoxyhexanoic acid. The quantities used were: 20 g. of sodium, 73 ml. of absolute ethanol, 17.25 g. of methyl malonate and 30.4 g. of 1-bromo-4,6-diphenoxyhexane. The distillation under reduced pressure gave the main fraction boiling at 205–240°/1 mm., weight 25 g. Hydrolysis of this impure product with 43 ml. of 30% sodium hydroxide, followed by decarboxylation gave a residue which boiled at 243–245°/1 mm.; yield 12.8 g. (44.7%).

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.2; H, 7.3; neut. equiv. 328. Found: C, 73.0; H, 7.8; neut. equiv. 325.

S-Benzylisothiouronium salt of 6,8-diphenoxyoctanoic acid. The procedure used was that described for the preparation of the *S*-benzylisothiouronium salt of 6,8-diphenoxyhexanoic acid. The m.p. of the solid product was 130–131°.

Anal. Calcd. for $C_{28}H_{34}O_4N_2S$: C, 67.9; H, 6.8; N, 7.6; S, 6.4. Found: C, 67.6; H, 6.7; N, 7.8; S, 5.9.

(b) *From 4,6-diphenoxyhexanoic acid.* A mixture of 4,6-diphenoxyhexanoic acid (9.8 g.) and benzyl hydrogen succinate (17.2 g.) in methanol (90 ml.), which contained 0.08 g. of sodium, was electrolyzed (0.8 amp., faradays passed *ca.* 1.5 times theoretical). A considerable amount of a colorless polymer began to separate from the electrolyte at an early stage in the electrolysis. After the electrolysis the alkaline cell contents were acidified and then evaporated. The residue was separated in the usual way into acidic and neutral fractions. Distillation of the latter gave three fractions: (i) A liquid (2.6 g.) b.p. 70–90°/0.3 mm. (ii) A fraction (2.65 g.) b.p. 150–180°/0.3 mm. which partly solidified. (iii) A liquid (7.4 g.) b.p. 210–250°/0.3 mm. Fraction (iii) and sodium hydroxide (4.0 g.) in water (8 ml.) and methanol (26 ml.) were boiled under reflux for 10 hr. An excess of alkali was then neutralized by 2*N* hydrochloric acid, the methanol was distilled off and the aqueous solution was extracted with ether. Evaporation of ether extract yielded a resinous product (1 g.). The ether insoluble material was treated with an excess of 30% hydrochloric acid and the resulting acid was extracted with ether. The residue left on evaporation of ether was distilled, giving 2.5 g. (32.4%) of 6,8-diphenoxyoctanoic acid, b.p. 234°/0.4 mm. Its *S*-benzylisothiouronium salt prepared as in (a) melted at 130–131° undepressed on admixture with a sample of the *S*-benzylisothiouronium salt prepared in (a). Fraction (ii), crystallized from petroleum ether (b.p. 50–70°), had m.p. 39°, undepressed on admixture with a specimen of benzyl adipate.

Acknowledgment The author wishes to acknowledge grants from the Rockefeller Foundation, New York, and Conselho Nacional de Pesquisas, Rio de Janeiro, and is also grateful to Prof. Heinrich Hauptmann for his interest and a critical reading of this paper.

SAO PAULO, BRAZIL

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER AND GOODRICH-GULF CHEMICALS, INC.]

Deuterio 1,3-Butadienes Derived by Reductive Dechlorination

DAVID CRAIG AND R. B. FOWLER

Received June 16, 1960

1,3-Butadiene-d_6, 1,3-butadiene-2,3-d_2, 1,3-butadiene-2-d_1 and 1,3-butadiene-1-d_1 have been prepared. The method of synthesis involves the reduction of mono-, di- and hexachloro-1,3-butadienes, and 1,4-dichloro-2-butyne with zinc and deuterium oxide. The reduction is catalyzed by cupric chloride as well as by sodium iodide. It was also applied to three dichlorobutenes. Dioxane, as previously reported, is a convenient solvent for the reaction but actually no solvent other than water is required. The use of maleic anhydride and gas phase chromatography (propylene carbonate column) for the analysis of 1,3-butadiene is described.

As part of an extensive program in these laboratories for the preparation of a variety of deuterated polymers, interest was recently focused on the preparation and stereospecific polymerization of several deuterio 1,3-butadiene monomers, *viz.*, butadiene-2-d_1, butadiene-2,3-d_2, and butadiene-d_6. This paper is concerned with the preparation of these monomers. The stereoregular polymerization[1a] of the monomers and the infrared spectra[1b] of the polymers will be presented elsewhere.

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[1] (a) H. Tucker, Belgian Patent 575,671, February 13, 1959, and paper to be submitted. (b) M. A. Golub and J. J. Shipman, *Spectrochim. Acta*, in press.

Morse and Leitch[2] have reported the synthesis of 1,3-butadiene-d_6 in 80% yield by the reaction of hexachlorobutadiene with deuterium oxide and zinc dust (Reaction 1). We have attempted their

$$6D_2O + 6Zn + Cl_2C{=}C(Cl){-}C(Cl){=}CCl_2 \longrightarrow D_2C{=}CDCD{=}CD_2 + 6Zn(OD)Cl \quad (1)$$

directions, including the use of dioxane as solvent, without observing more than low yields of diene and finding instead considerable amounts of 1-buten-3-yne and 1,3-butadiyne. A study with water as well as with deuterium oxide revealed that good yields of diene can be expected if sodium iodide, a reagent previously used in dehalogenations by Leitch and Morse,[3] is added to the reaction mixture. We can note too that they found hexachloropropene to form the hydrogen-poor products[1] 1-propyne and propadiene when used in place of hexachlorobutadiene in the absence of sodium iodide. We have found that the action of sodium iodide is enhanced by cupric chloride as a co-catalyst and by cupric chloride alone. As revealed by our studies the replacement of chlorine with hydrogen (hydrogenolysis) is favored by excess zinc and other conditions causing fast reaction including the presence of catalysts. The formation of hydrogen-poor products is favored by slow reaction just as though non-reductive dehalogenation would eventually occur. Alternatively, the same dehalogenation products might form by dehydrohalogenation of initially formed hydrogenolysis products. The impurities, including the acetylenes, were removed by purifying the 1,3-diene by the sulfone method. The diene then polymerized satisfactorily.[1]

We have not isolated partially dechlorinated derivatives from the reduction mixture of hexachlorobutadiene but have studied the reductive dechlorination of postulated intermediate chlorides as follows: chloroprene, *cis*- and *trans*-1-chloro-1,3-butadienes, 2,3-dichloro-1,3-butadiene, 1,4-dichloro-2-butyne, *cis*- and *trans*-1,4-dichloro-2-butenes, and 3,4-dichloro-1-butene. All of these react with water in the mixture to give good yields of 1,3-butadiene or with deuterium oxide as the hydrogen source to give the expected partially deuterated dienes with the exception, of course, of the dichloro butenes where only dehalogenation occurs.

The by-products vary somewhat from one starting chloride to another. Thus, with the monochloro dienes and the dichloro butenes the derived 1,3-butadiene is nearly pure. With hexachlorobutadiene the main byproduct is 1-buten-3-yne, with some 1,3-butadiyne and very small amounts of 2-butyne. Roedig and coworkers[4] reported the first two hydrocarbons as products of the alcoholic zinc dehalogenation of hexachlorobutadiene.

The most abundant impurity in the diene derived from 1,4-dichloro-2-butyne is 2-butyne but, among many products, 1,2-butadiene is also present, presumably formed according to Reaction

$$2H_2O + 2Zn + ClCH_2{-}C{\equiv}C{-}CH_2Cl \longrightarrow CH_2{=}C{=}CH{-}C(H)H_2 + 2Zn(OH)Cl \quad (2)$$

2 by a combination of two types of reductive dehalogenation. 2-Butyne is formed by hydrogenolysis and, as expected, the yield is greater than when the starting chloride is hexachlorobutadiene. 2,3-Dichloro-1,3-butadiene and deuterium oxide lead to 1,3-butadiene-2,3-d_2 and impurities identical, according to mass spectra, to those derived from the dichloro-2-butyne and deuterium oxide. The main product is 1,3-butadiene-2,3-d_2 and the impurities are 1,2-butadiene-3,4-d_2 and 2-butyne-1,4-d_2.

The 1,4-dichloro 2-butenes and 3,4-dichloro-1-butene reacted with deuterium oxide to give high yields of deuterium-free 1,3-butadiene. We know from this that neither hydrogenolysis nor hydrogen isotope exchange occurred.

The mechanism by which reductive dechlorination occurs is still not clear. Clarification must await knowledge of the stereospecificity of the replacement, and this feature is now under study. Thus it will be important to find if the configuration of the monodeuterio-1,3-butadienes derived from the 1-chlorobutadiene isomers can be related to the structures of the starting materials.

EXPERIMENTAL

Hexachloro-1,3-butadiene was crystallized from pentane after which it melted at −19 to −18°. *2,3-Dichloro-1,3-butadiene*, m.p. −40°, was prepared by the reaction of potassium hydroxide with mixed 1,2,3,4-tetrachlorobutanes and was crystallized from pentane. *1,4-Dichloro-2-butyne* was purchased from the General Aniline & Film Corporation. It melted at −34.5°. Part of the *cis*- and *trans-1,4-dichloro-2-butenes* and *3,4-dichloro-1-butene* were prepared by the vapor phase chlorination of 1,3-butadiene by Drs. Floyd Ramp, Robert Fawcett, Eugene Sehm, John Wenrick, and associates of these laboratories. After careful fractionation, the *1,4-dichloro-cis-2-butene* melted at −50°. Mislow and Hellman[5] reported −48° as the melting point of the *cis*-dichloride derived from *cis*-2-butene-1,4-diol. We have confirmed their synthesis and melting point for the *cis*-dichloride. They reported the *trans*-dichloride to melt at +1° and prepared it by passing streams of chlorine and butadiene (1:3 ratio) at Dry Ice temperature into carbon tetrachloride. As this solvent freezes at about −23°, the conditions used by them are not entirely clear. However, there is no doubt about their assignment of configuration. Our *trans*-dichloride, prepared in chloroform at −70°, melted at +2.5° after crystallization from pentane.

1,3-Butadiene-d_6. A 3-l. flask fitted with a paddle-type stirrer, thermometer, dropping funnel, and helices-filled fractionating column was charged with 570 g. of azeotropically-dried dioxane, 480 g. (6.6 g.-atoms) of 90% zinc

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[2] A. J. Morse and L. C. Leitch, *J. Org. Chem.*, **23**, 990 (1958).

[3] L. C. Leitch and A. J. Morse, *Can. J. Chem.*, **30**, 924 (1952).

[4] A. Roedig and A. Kling, *Ann.*, **580**, 20 (1953); A. Roedig, G. Voss, and E. Kuchinske, *Ann.*, **580**, 24 (1953).

[5] K. Mislow and H. M. Hellman, *J. Am. Chem. Soc.* **73**, 245 (1951).

dust, and 10 ml. of 99.5% deuterium oxide. The apparatus was maintained under an atmosphere of nitrogen. Distillation was effected until 60 g. of distillate had been collected. Anhydrous potassium carbonate was added to the distillate to salt out the dioxane, the water layer was separated and distilled to give a forerun of 2.2 g. of m.p. 3.4° and a second fraction of 3.2 g. which melted at 3.8°. The dioxane-zinc dust mixture was thus shown to be substantially free of water.

The fractionating column was replaced with a reflux condenser, the upper end of which was connected in turn to an air-cooled receiver and a Dry Ice cooled trap. A freshly prepared mixture of 4.0 g. sodium iodide, 24.0 g. cupric chloride, and 132 g. (6.6 moles) of 99.5% deuterium oxide was then added and the stirrer started. The temperature promptly rose to 41°. The mixture was quickly heated to reflux at 86° and the addition of 261 g. (1.00 mole) of hexachlorobutadiene dissolved in 340 g. of water-free dioxane was started. The evolution of butadiene was immediate but gradually became less vigorous. During 2 hr., 412 g. of the hexachlorobutadiene-dioxane solution or 0.69 mole of the hexachloride was added. The condensate (A) in the Dry Ice trap which then weighed 30.9 g. (0.52 mole C_4D_6 or 75% yield) was set aside and a second trap attached. The remaining portion (0.31 mole) of hexachlorobutadiene was added during 5 hr. during which time 9.0 g. (B) of condensate was collected. Condensate (A) was found to be 94% reactive with excess maleic anhydride during 1 hr. at 100° which indicates a yield of 70% of 1,3-butadiene-d_6. Only 72.5% of condensate (B) reacted with maleic anhydride. The total yield of diene reactive with maleic anhydride thus was 59%.

The portions of condensates (A) and (B) not reacting with maleic anhydride during diene analysis were evaporated to a single Dry Ice cooled trap and a mass spectrum analysis run on the condensate. This showed it to be mainly 1-buten-3-yne-d_4 with very minor amounts of 1,3-butadiyne-d_2.

The crude perdeuterio butadiene, condensates (A) and (B), was treated in a bomb with excess sulfur dioxide in the presence of a mixture of hydroquinone and phenyl-2-naphthylamine. The unchanged starting materials were allowed to escape, the sulfone taken up in hot methanol, and the solution filtered to remove small amounts of polymer and cooled to give a crystalline product which melted at 63.8°. The corresponding perprotio derivative, similarly purified, melted at 62.2°.

The decomposition of the sulfone was conducted in nitrogen stream at 130°, the sulfur dioxide being removed by scrubbing with 25% potassium deuteroxide. The hydrocarbon was dried over potassium carbonate and distilled over calcium hydride. It boiled at about 0.5° lower than research grade 1,3-butadiene-h_6 which boils at $-4.5°$. Mass spectrum analysis showed 97.6% of the hydrogen atoms present to be deuterium and 2.4% to be protium. This corresponds to about 85.7% C_4D_6 and 14.3% C_4D_5H.

The reaction of hexachlorobutadiene in dioxane with zinc dust and deuterium oxide according to the procedure of Morse and Leitch[2] gave about 57% of a mixture of C_4 hydrocarbons, 29% of which reacted with maleic anhydride to give the butadiene adduct, m.p. 104–105°. The hydrocarbon not reacting with maleic anhydride was recovered and by mass spectrum analysis found to consist of approximately 90% 1-buten-3-yne-d_4 and 10% 1,3-butadiyne-d_2.

1,3-Butadiene-d_6 can be prepared similarly in the absence of an organic solvent. A 500-ml., three necked flask was fitted with a paddle-type stirrer, thermometer, nitrogen inlet, dropping funnel, heating mantle, and reflux condenser, the top of which was connected to a Dry Ice trap. Sixty grams of zinc dust (90%) was added to the flask followed by a mixture of 0.5 g. sodium iodide, 3.0 g. cupric chloride, and 100 g. of 99.5% deuterium oxide. The stirrer was started, the reaction mixture quickly heated to reflux and 32.5 g. (0.125 mole) hexachlorobutadiene added during 1 hr. Refluxing was continued for 30 min. The yield of condensate amounted to 6.3 g. or, calculated on the hexachloride, to an 84% yield, 90% of which was reactive toward maleic anhydride. The addition of 1.5 ml. of ethanol increased the rate of diene evolution but had no effect on the rate when dioxane was the solvent. With water as the solvent and a small amount of ethanol and in the absence of sodium iodide and cupric chloride, the yield of hydrocarbon amounted to 24%. Maleic anhydride analysis followed by chromatographic analysis of the unchanged hydrocarbon showed the product to contain 44% 1,3-butadiene, 35% 1-buten-3-yne, and 19% 1,3-butadiyne. Hydrocarbons identified by mass spectrum analysis on the "trapped" peaks from the chromatograph were 1,2-butadiene, 2-butyne, *cis*-2-butene, and *trans*-2-butene. The chromatograph used was a Kromo-Log, Model K-1, purchased from the Burrell Corporation, Pittsburgh, Pa. The stationary phase was propylene carbonate deposited on two parts pulverized firebrick. It was 2.5 m. long and was operated at 25° with helium as the carrier gas at 40 ml. per min. Very small peaks were also observed in the chromatogram at the correct positions for cyclobutene, *n*-butane, 1-butene, 1-butyne, and acetylene. Table I shows the retention times for these hydrocarbons and other compounds of interest, such as 1,3-butadiene-d_6, the retention time of which is substantially the same as that of 1,3-butadiene-h_6.

TABLE I

RELATIVE RETENTION TIMES ON PROPYLENE CARBONATE COLUMN AT 25°

1,3-Butadiene 3.5 min. (absolute)	1.00
1,3-Butadiene-d_6	1.00
CO_2	.16
Isobutane	.16
n-Butane	.24
Acetylene	.39
1-Butene	.41
2-Methyl-1-propene	.48
trans-2-Butene	.49
cis-2-Butene	.61
Cyclobutene	.83
Propyne	1.22
Vinyl chloride	1.29
1,2-Butadiene	1.35
Methyl chloride	1.44
1-Butyne	2.33
Ethyl chloride	3.20
1-Buten-3-yne	3.30
2-Butyne	4.10
2-Methyl-1-butene-3-yne	6.00
Butatriene(?)	6.00
1,3-Butadiyne	13.00

The reduction of 141.5 g. (1.09 moles) of *1,4-dichloro-2-butyne* was conducted in dioxane (260 ml.) solution with 210 g. (2.9 g.-atoms) of 90% zinc dust and 80 g. (4.4 moles) of water in the presence of 10.5 g. sodium iodide and 10.5 g. cupric chloride. The procedure was substantially the same as for the reduction of hexachlorobutadiene. The dichloro-2-butyne is very reactive and it was added in admixture with 140 ml. of dioxane (total dioxane, 400 ml.) during 2.5 hr. after which the mixture was refluxed 0.5 hr. longer. The yield of hydrocarbon was 55.1 g. (93%) which by maleic anhydride–gas chromatographic analysis was 89% 1,3-butadiene, 7.3% 2-butyne, 3.2% 1,2-butadiene, and 0.36% 2-butene. A minor peak possibly assignable to butatriene[6] was also noticed in the chromatogram of the 1,3-butadiene-free hydrocarbon and in the reflux condenser of the reaction

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(6) W. M. Schubert, T. H. Liddecoet, and W. A. Lanka, *J. Am. Chem. Soc.*, 76, 1929 (1954).

flask there was a light deposit of polymer, with a satisfactorily analysis (in the case of an experiment with deuterium oxide) for $(C_4D_4)_x$.

The reactions of the diene samples with maleic anhydride were conducted in tared screw-capped, 0.5 ounce bottles. The bottles were sealed with a short rubber stopper held in place with the cap in which a hole had been drilled for sampling and, occasionally, for charging with a needle and syringe. The reaction of butadiene (0.02 mole) of high purity was usually conducted with about 10% excess maleic anhydride and with low purity samples with at least 100% excess dienophile. For inhibiting polymerization 0.01 g. of picric acid and 0.01 g. of di-*n*-amylamine were added just prior to the addition of the sample which was usually charged last and at about −50°. The main reaction was allowed to start at about 30° behind a barricade. After the main part of the reaction, which is vigorous for high purity samples, had occurred the reaction was completed by heating in a 100° oven, usually for 1 hr. For recovery of unchanged hydrocarbon the bottle was evacuated to constant weight at room temperature to a refrigerated trap and the per cent of the sample reacted calculated as the butadiene content.

Acknowledgment. D. W. Beesing and Caroline A. McKalen carried out the vapor phase chromatography studies reported here; the mass spectrometry was done by E. H. Rowe and Dwain E. Diller. The support of these specialists often went beyond their particular skills.

BRECKSVILLE, OHIO

[CONTRIBUTION FROM THE CHEMICAL DIVISION, DENVER RESEARCH INSTITUTE, UNIVERSITY OF DENVER]

Heptyl and Nonyl Derivatives of Bicyclohexyl and *m*-Tercyclohexyl[1]

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Received June 16, 1960

The syntheses and properties of four alkylpolycyclohexyls are reported.

Work in this laboratory, resulting in the synthesis of many new alkylbiphenyls and alkylterphenyls, has made available a potential source of numerous alkylbicyclohexyl and alkyltercyclohexyl compounds. Accordingly we have synthesized gallon quantities of four new hydrocarbons for use as experimental fuels, namely, 4-*n*-heptylbicyclohexyl, 4-*n*-nonylbicyclohexyl, 4′-*n*-heptyl-*m*-tercyclohexyl, and 4′-*n*-nonyl-*m*-tercyclohexyl.

The literature contains only a few references to alkylbicyclohexyl compounds, the most extensive being the work of Goodman and Wise,[2] who prepared a series of 2-alkylbicyclohexyls by the hydrogenation of the corresponding 2-alkylbiphenyls. No alkyltercyclohexyls compounds have been reported.

The alkylbicyclohexyls were obtained by acylating biphenyl with the appropriate acid chloride according to the method of Long and Henze,[3] hydrogenating the resulting ketone to an alkylbiphenylylcarbinol, dehydrating the alcohol to the alkenylbiphenyl, and finally hydrogenating the alkenylbiphenyl to the desired alkylbicyclohexyl. As the acylation of biphenyl has been established as occurring in the 4-position,[4] the 4-alkylbicyclohexyls were thus prepared.

It is interesting to note that whereas the preparation of phenylmethylcarbinol by the hydrogenation of acetophenone can yield large amounts of ethylbenzene unless conditions are carefully controlled,[5] a similar reaction was not noted during the hydrogenation of 4-heptanoyl- or 4-nonanoylbiphenyl.

The alkyl-*m*-tercyclohexyls were prepared by the hydrogenation of the 4′-alkenyl-*m*-terphenyls, the preparation of which has already been described.[6]

The complete hydrogenation of alkylbiphenyls and alkylterphenyls to the desired alkylbicyclohexyls and alkyltercyclohexyls was difficult and was never accomplished in a single step. In practice, the alkenylpolycyclohexyl compound was hydrogenated until no more hydrogen was absorbed. The product showed evidence for incomplete saturation by a slight fluorescence under ultraviolet light irradiation and by the formation of a light red color when treated with aluminum chloride and chloroform, this color becoming more intense and shifting towards blue or purple as the degree of unsaturation increased. The product was rehydrogenated until the final hydrocarbon showed no ultraviolet light fluorescence and gave only a slight yellow color when treated with aluminum chloride and chloroform. It is estimated that the hydrogenation was at least 98% completed in the first step.

All of the four alkylpolycyclohexyl compounds prepared could exist in *cis-trans* configurations. However, no attempt was made to isolate the var-

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[1] This research was supported in whole by the United States Air Force under contract AF 33(600)-37474, monitored by the Propulsion Laboratory, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

[2] I. A. Goodman and P. H. Wise, *J. Am. Chem. Soc.*, **73**, 850 (1951).

[3] L. M. Long and H. R. Henze, *J. Am. Chem. Soc.*, **63**, 1939 (1941).

[4] S. L. Silver and A. Lowy, *J. Am. Chem. Soc.*, **56**, 2429 (1934).

[5] V. N. Ipatieff and B. B. Corson, *J. Am. Chem. Soc.*, **61**, 3292 (1939).

[6] J. J. E. Schmidt, J. A. Krimmel, and T. J. Farrell, Jr., *J. Org. Chem.*, **25**, 252 (1960).