mixture disappeared. After vigorous shaking, 25 ml. of pentane was added to minimize emulsion formation; and shaking was continued. The organic layer was washed with 5% sodium bicarbonate solution and water and dried with Drierite. The bulk of the solvent was slowly boiled off on a steam plate. Independent experiments showed that no loss of products or reactants occurred. The remaining solution was analyzed by v.p.c. In some cases, 0.200 ml. of *n*-hexadecane was added during washing as an internal standard for determination of yield by v.p.c.

The one exception to the general procedure occurred in the alkylation of cumene where a two-step alkylation was required to ensure complete reaction.[26] Cumene (50 ml.) was placed in flask equipped as above. After cooling to −15°, aluminum bromide (2.26 g., 0.00424 mole) was introduced. One-half minute thereafter, *n*-dodecyl bromide (6.00 g., 0.0241 mole) was added over a period of 15 seconds. The temperature rose to −11° but returned to −15° within 0.5 minute. After 8 minutes, a 5-ml. sample was removed and analyzed by the above procedure. Reaction was 84% complete. After 11 minutes, the entire mixture was quickly transferred to a freshly prepared solution of aluminum bromide (4.62 g., 0.00866 mole) in 65 ml. of cumene at −15°. Twenty-four minutes later, a sample was removed for analysis. Reaction was 98% complete.

Several preparative scale alkylations were run in the manner just described. The products were distilled. In the case of dodecylbenzene studies, the boiling range was 118–159° (2 mm.). The yields were 88–90%.

Isomerization of Secondary Dodecylbenzenes.—Mixtures of secondary dodecylbenzenes were isomerized to the equilibrium composition in both benzene and petroleum ether. The following describes the study in benzene. A mixture of composition 20.0% 2-phenyl-, 17.1% 3-phenyl- and 62.9% 4- + 5- + 6-phenyldodecane (2.00 g., 0.00812 mole) was placed in 25 ml. of benzene at 25° contained in a flask fitted with a stirrer, thermometer and drying tube. Aluminum bromide (1.017 g., 0.0019 mole) then was added. Hydrogen bromide gas was bubbled through the solution for 1 minute. Samples were withdrawn by the above technique at 13, 100 and 370 minutes. Analysis by v.p.c. showed that all samples had the equilibrium composition. Dealkylation also occurred.

Acknowledgment.—The author is indebted to Professor Saul Winstein and Doctors Everett Clippinger and Maurice Schlatter for helpful suggestions during the preparation of the manuscript.

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[26] In the alkylations using these substituted benzenes, the initial reaction was very rapid; but as product was formed, a sharp deceleration or complete cessation of alkylation occurred. Data included in Table III illustrate this behavior. The stability of aluminum halide-aromatic complexes increases as additional alkyl substitution is introduced.[23] Presumably, this rapid decrease in rate reflects a reduction in the efficiently of the catalyst as it becomes complexed with the more highly substituted products.

[CONTRIBUTION FROM CALIFORNIA RESEARCH CORPORATION, RICHMOND 1, CALIF.]

Alkylaromatics. Part II. A Study of the Transfer of Alkyl Groups by Aluminum Bromide–Hydrogen Bromide Catalysis[1]

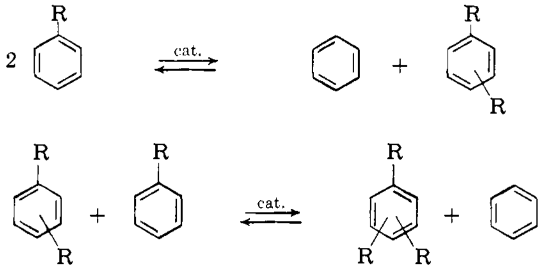
BY SAMUEL H. SHARMAN

RECEIVED MARCH 6, 1962

Dodecylcumenes and dodecylethylbenzenes of high primary isomer content have been prepared by Friedel–Crafts alkylations with *n*-dodecyl bromide. Treatment of these products with aluminum bromide and hydrogen bromide in a large excess of benzene causes selective transfer of secondary alkyl groups. Dodecylcumenes were converted completely to dodecylbenzenes.

Introduction

Disproportionation of alkylbenzenes in the presence of aluminum halide–hydrogen halide or other Lewis acid-type catalysts has long been known.[2] Numerous investigators have reported that under relatively mild conditions, migration of straight chain alkyl groups occurs without rearrangement.[3–9] Brown and Smoot[7] demonstrated that transfer of secondary alkyl groups is much faster than that of primary side chains, *i.e.*, isopropyl >> *n*-propyl. The previous paper in this series[10] reported that Friedel–Crafts alkylation of aromatics occurs with relatively little rearrangement if alkyl-substituted benzenes are employed. In the present work, we have made use of these facts to produce, by a two-stage process, alkylbenzenes with increased primary side chain attachment.



Results and Discussion

Aluminum bromide catalyzed alkylation of ethylbenzene at −20° with *n*-dodecyl bromide produced a dodecylethylbenzene mixture in which about 70% was *n*-dodecylethylbenzene.[10] This alkylation mixture was mixed with a large excess of benzene at 6° containing aluminum bromide and hydrogen bromide. Reaction was followed by v.p.c. analysis of samples withdrawn periodically and quenched by hydrolysis. Alkyl transfer was significant within 7 minutes as shown by the ap-

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[1] Presented in part before the Division of Petroleum Chemistry, 141st Meeting of the American Chemical Society, March 20–29, 1962, Washington, D. C.

[2] D. V. Nightingale, *Chem. Revs.*, **25**, 329 (1939).

[3] R. Heise and A. Tohl, *Ann.*, **270**, 155 (1892).

[4] G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935).

[5] R. E. Kinney and L. A. Hamilton, *J. Am. Chem. Soc.*, **76**, 786 (1954).

[6] A. P. Lien and D. A. McCaulay, *ibid.*, **75**, 2411 (1953).

[7] H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

[8] S. G. Clark and J. A. Dixon, *J. Org. Chem.*, **23**, 1628 (1958).

[9] (a) R. M. Roberts, G. A. Ropp and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 1764 (1955); (b) R. M. Roberts, S. G. Brandenberger and S. G. Panayides, *ibid.*, **80**, 2507 (1958); (c) R. M. Roberts, Y. W. Han, C. H. Schmid and D. A. Davis, *ibid.*, **81**, 640 (1959); (d) R. M. Roberts and J. E. Douglass, *Chemistry & Industry*, 926 (1959); (e) R. M. Roberts and S. G. Brandenberger, *ibid.*, 227 (1955).

[10] S. H. Sharman, Part I, *J. Am. Chem. Soc.*, **84**, 2945 (1962).

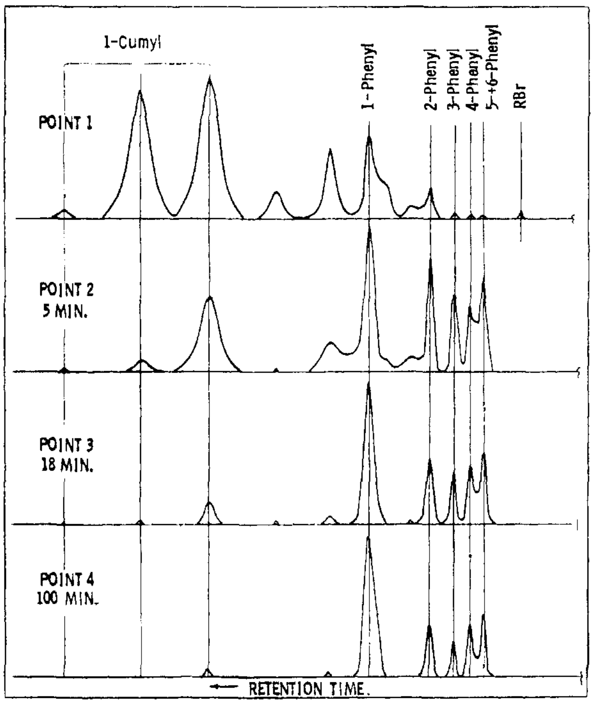
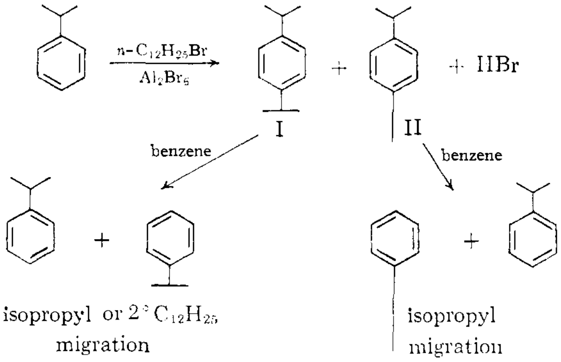


Fig. 1.—Phenyldodecanes from cumyldodecanes.

pearance of peaks representing dodecylbenzenes and the reduction in size of peaks characteristic of dodecylethylbenzenes. After 4 hours, the mixture contained only primary dodecylethylbenzene (*ca.* 52%) and dodecylbenzenes (*ca.* 48%) of which 31.4% was primary. Thus, all the alkylation products with the labile secondary side chain had been converted to secondary alkylbenzenes by transfer of either an ethyl or secondary dodecyl group to benzene. The data of Brown and Smoot[7] suggest that most of the product resulted from transfer of the secondary group. That this was indeed the case is supported by the fact that about 75% of the *n*-dodecylethylbenzene did not undergo reaction in the time required for complete transfer of secondary groups. The remaining 25% which did become involved in the relatively sluggish transfer of a primary group produced the 1-phenyldodecane found.[11]

The entire alkylation product can readily be converted to a mixture of alkylbenzenes if each aromatic nucleus contains at least one secondary alkyl group. For example, alkylation of cumene at −15° with *n*-dodecyl bromide gave a mixture of dodecylcumenes in which the primary isomer II was present to the extent of at least 72%. Small quantities of dodecylbenzenes also were produced as a result of alkylation of the benzene formed by disproportionation of cumene.[10] Through transfer of a mobile secondary group (either isopropyl or secondary dodecyl), the two types of dodecylcumenes I and II were converted to the corresponding dodecylbenzenes.



In Fig. 1 are shown in order from top to bottom v.p.c. traces of samples consecutively withdrawn for analysis. The upper trace (point 1) indicates the composition of the mixture after alkylation was complete. The second trace (point 2) is that of a sample removed 5 minutes after alkyl transfer had been initiated by treating the alkylation mixture with fresh aluminum bromide and hydrogen bromide in a large excess of benzene. Clearly the primary and secondary dodecylcumene peaks have begun to disappear, and the peaks representing the corresponding monoalkylbenzenes have grown. The process continued until in 100 minutes (point 4), the mixture is composed almost entirely of dodecylbenzenes. Except for the traces of dodecylcumenes, the v.p.c. curve of point 4 is completely typical of those obtained in our studies of the alkylation of benzene with *n*-dodecyl bromide.[10]

Thus, we have succeeded in preparing straight chain alkylbenzenes of high primary isomer content by the Friedel–Crafts technique by taking advantage of the increased ability of substituted benzenes to undergo alkylation in a primary fashion. The resulting improved composition was then maintained while alkyl groups were transferred to benzene. Perhaps a similar treatment using such aromatic hydrocarbons as diisopropylbenzene would provide even more striking results since increased substitution of the benzene nucleus seems to reduce the amount of rearrangement accompanying alkylation.[10,12]

Experimental

Alkylation experiments were described previously.[10] A typical example of the alkyl transfer reaction is reported. A 35-ml. sample of the alkylation product mixture (containing 1.92 g., 0.0066 mole, of dodecylcumene) was transferred to 250 ml. (2.7 moles) of benzene at 6° containing 5.79 g. (0.0109 mole) of aluminum bromide. Hydrogen bromide (approximately 2 g., 0.025 mole) was bubbled through the solution in 1 minute; 20-ml. samples were withdrawn at 5, 18 and 100 minutes, hydrolyzed and analyzed by v.p.c. according to the method described earlier.[10]

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[11] Primary–secondary dodecylbenzene ratio measured, 31.4:68.6; calculated, 34.66.

[12] C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6249 (1956).

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

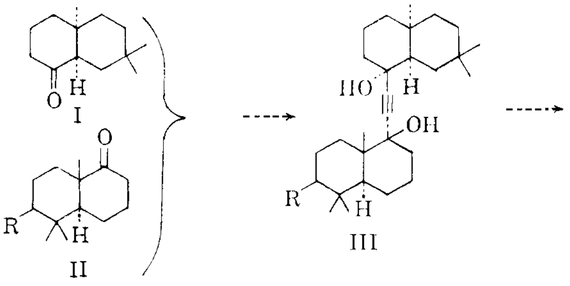
Syntheses in the Terpene Series. XI.[1] Model Experiments with *sym*-Dicyclohexylethane Derivatives[2]

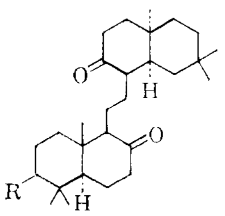
BY EUGENE GHERA, MARTIN GIBSON[3] AND FRANZ SONDHEIMER

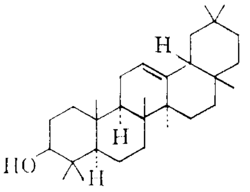
RECEIVED JANUARY 30, 1962

The conversion of bis-(1-hydroxycyclohexyl)-acetylene (VI) to 1,2-bis-(2-ketocyclohexyl)-ethane (XI) by two different routes is described, a transformation which serves as a model for a projected synthesis of triterpenes related to β-amyrin. In addition, related experiments with *sym*-dicyclohexylethane derivatives are reported.

Syntheses of the bicyclic ketones I[4] and II (R = H or OH)[5] have been described in previous parts of this Series. It was our intention to utilize these substances for the total synthesis of triterpenes related to β-amyrin (V), *e.g.*, through conversion to the "mixed" acetylenic 1,4-diol III, followed by successive transformation to the diketone IV, treatment with methylmagnesium bromide and acid cyclization. As a model for the conversion of III to IV, it was decided first to study methods for the analogous transformation of bis-(1-hydroxycyclohexyl)-acetylene (VI) to 1,2-bis-(2-ketocyclohexyl)-ethane (XI), since the acetylenic diol in this series can be obtained readily in quantity. In this paper we describe two methods of synthesis of the diketone XI from the acetylenic diol VI, as well as the results of related experiments designed to bring about this transformation. One of these methods was subsequently applied successfully to the synthesis of diketones of type IV, as will be reported in a later paper of this series.




IV


V

The acetylenic diol VI was dehydrated smoothly to dicyclohexenylacetylene (VII) by means of potassium bisulfate at 200°, essentially as described previously.[6] It has been shown that per-acids attack double bonds much more rapidly than triple bonds.[7a] As expected, oxidation of the dienyne VII with 2.3 molar equivalents of perbenzoic acid readily yielded 60% of the acetylenic diepoxide VIII, the structure of which is based on the elemental composition and the absence of appreciable absorption in the ultraviolet. The compound proved to be a liquid, and most probably consists of a mixture of *meso* and racemic forms.[8]

The diepoxide VIII in ethanol was hydrogenated first over a Lindlar lead-poisoned palladium–calcium carbonate catalyst,[9] and then (when uptake of hydrogen had become very slow) over a palladium–charcoal catalyst. Chromatography of the resulting mixture on alumina yielded *ca.* 25% of the di-*sec*-diol IX as a mixture of two stereoisomers, which could be separated into the pure components, m.p. 98–99° (isomer A) and 115–116° (isomer B).[10] In addition, the liquid secondary mono-ol X was isolated in *ca.* 30% yield. The structures of these hydrogenation products follow from their behavior on oxidation. The fact that secondary alcohols rather than saturated oxides or tertiary alcohols are formed is presumably due to the fact that cleavage of the weak propargylic (or allylic) carbon–oxygen bond occurs readily and prior to complete saturation of the acetylenic linkage. The loss of oxygen leading to the mono-ol X was unexpected, but finds some analogy in the literature.[12]

Oxidation of either isomer of the di-*sec*-diol IX (or of the mixture of isomers) with chromium

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[1] For Part X, see, N. Danieli, Y. Mazur and F. Sondheimer, *Tetrahedron Letters*, 310 (1961).

[2] This work was supported in part by a grant from Mr. Arthur B. Krim, New York.

[3] Weizmann Fellow, 1958–1959. Present address: Department of Chemistry, Faculty of Technology, University of Manchester, England.

[4] F. Sondheimer and S. Wolfe, *Can. J. Chem.*, **37**, 1870 (1959).

[5] F. Sondheimer and D. Elad, *J. Am. Chem. Soc.*, **79**, 5542 (1957); **80**, 1967 (1958).

[6] (a) P. S. Pinkney, G. A. Nesty, D. E. Pearson and C. S. Marvel, *ibid.*, **59**, 2666 (1937); (b) H. H. Inhoffen and G. Quinkert, *Ber.*, **87**, 1418 (1954).

[7] See R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths Scientific Publications, London, 1955; (a) pp. 33–34 and references cited there; (b) p. 35.

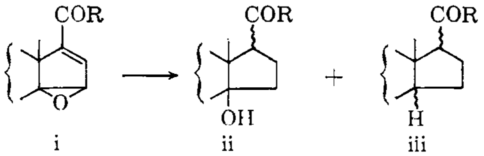
[8] No stereochemical assignments are implied in formulas VIII *et seq.*

[9] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

[10] Neither of these isomers appears to be identical with the isomer of IX (m.p. 139°) reported to be formed by hydrogenation of 2,2'-dihydroxybibenzyl.[11]

[11] S. C. Bhattacharyya, *J. Indian Chem. Soc.*, **33**, 545 (1956).

[12] *Cf.* the catalytic hydrogenation of steroidal 14β,15β-epoxy-Δ^{16}-etienic acid esters (i, R = OCH_3) and pregnen-20-ones (i, R = CH_3) to the desoxy compounds iii in addition to the 14β-alcohols ii.[13]



[13] P. A. Plattner, L. Ruzicka, H. Heusser, J. Pataki and K. Meier, *Helv. Chim. Acta*, **29**, 942 (1946); P. A. Plattner, L. Ruzicka, H. Heusser and E. Angliker, *ibid.*, **30**, 385 (1947); H. Heusser, N. Frick, E. V. Jensen and P. A. Plattner, *ibid.*, **32**, 1334 (1949).