

[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

The Lithium Aluminum Hydride Hydrogenolysis of 6-Hexylbenzanthrone¹

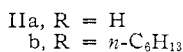
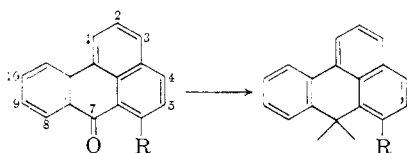
BY HERMAN E. ZIEGER² AND JOSEPH A. DIXON

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6-Hexylbenzanthrone was hydrogenolyzed by lithium aluminum hydride to 6-hexylbenzanthrene in 75% yield. Under the same conditions benzanthrone does not react. Hydrolysis with deuterium oxide of the lithium aluminum hydride reaction complex yielded non-deuterium-containing 6-hexylbenzanthrene. However, reduction with lithium aluminum deuteride followed by hydrolysis with ordinary water produced 7,7-dideuterio-6-hexylbenzanthrene. The rate of disappearance of ketone exceeds the rate of formation of hydrocarbon. A rationalization of this and other lithium aluminum hydride promoted hydrogenolyses is offered.

Introduction

In connection with a synthetic study, it was desired to convert 6-hexylbenzanthrone (Ib) to 6-hexylbenzanthrene (IIb). Since benzanthrone³ (Ia) is smoothly hydrogenolyzed to benzanthrene (IIa) in good yield by aluminum isopropoxide in isopropyl alcohol,^{4,5} this method was tried. When it failed, excess lithium aluminum hydride was



used to accomplish the hydrogenolysis in 75% yield. This is somewhat surprising, for benzanthrone (Ia) is not affected by lithium aluminum hydride under the same conditions. When the literature failed to provide a satisfactory rationalization of these observations, it was decided to study this reaction.

Experimental

Preparation of 6-Hexyl-7H-benz[de]anthracene-7-one.⁶⁻ A suspension of 115 g. of benzanthrone^{9,10} (0.50 mole) and 1.0 liter of anhydrous diethyl ether was treated with 0.94 liter of an ether solution of hexylmagnesium chloride, prepared from 36.5 g. of magnesium (1.50 moles) and 181 g. of hexyl chloride (1.50 moles), b.p. 70.0–70.8° (84 mm.), *n*_D²⁵ 1.4178. The black reaction mixture was refluxed for 24 hours and hydrolyzed with a mixture of acetic acid and ice.

The organic reaction products were distilled; the distillate, 162 g., was fractionally distilled through a spinning band column.¹¹ A 40.6% yield of 6-hexylbenzanthrone was obtained, b.p. 220–222° (0.25 mm.). Two recrystallizations from ethanol gave 47.1 g. of yellow needles (30%), m.p. 80.1–80.5°.

(1) Presented in part at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 14, 1959.

(2) American Petroleum Institute Fellow, 1957–1959.

(3) Systematic name: 7H-benz[de]anthracene-7-one.

(4) N. Campbell and A. A. Woodham, *J. Chem. Soc.*, 843 (1952).

(5) H. Dannenberg and H. J. Kessler, *Ann.*, **620**, 32 (1959).

(6) It has been shown conclusively that the Grignard reagent adds 1–4 to benzanthrone.^{7,8}

(7) G. Charrier and E. Ghigi, *Ber.*, **69**, 221 (1936).

(8) C. F. H. Allen and S. C. Overbaugh, *THIS JOURNAL*, **57**, 740 (1935).

(9) L. C. Macleod and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 62.

(10) Commercial benzanthrone is available from the Antara Chemical Co. After extensive purification (ref. 9), m.p. 174–175°.

(11) This column is manufactured by the Nester-Faust Co., Exton, Pa. The column length is 36 inches, the internal diameter is 11 mm. The band is a spiral of 300 mesh stainless steel screen.

Anal. Calcd. for C₂₃H₂₂O: C, 87.90; H, 7.00. Found: C, 87.97; H, 6.92.

Preparation of 6-Hexyl-7H-benz[de]anthracene.—Lithium aluminum hydride (7.0 g., 0.184 mole, 95+%, Metal Hydrides, Inc.) was dissolved in 200 ml. of anhydrous diethyl ether. An ether solution (250 ml.) of 6-hexylbenzanthrone (28.0 g., 0.089 mole) was added. The reaction mixture was refluxed for 7.25 hours; the excess lithium aluminum hydride was hydrolyzed with water and the salts were dissolved by addition of 125 ml. of hydrochloric acid. After separation, drying, concentration to 50 ml. and chilling to –5°, the ether phase yielded light tan prisms of 6-hexylbenzanthrene, 19.02 g., 71.1%, m.p. 85–87°. Chromatographic purification on alumina of the oil which resulted upon evaporation of the mother liquor yielded an additional 0.31 g. of 6-hexylbenzanthrene (1.15%) and 2.97 g. of unreacted 6-hexylbenzanthrone (10.6%). Several recrystallizations of the hydrocarbon from hexane yielded white prisms, m.p. 86.8–87.6°; ultraviolet spectrum in 95% ethanol,¹² λ_{max} mμ (log ε): 226.0 (4.59), 232.3 (4.64), 248.2 (4.22), 256.8 (4.16), 314.8 (3.93), 326.2 (4.011), 346.8 (3.99).

Anal. Calcd. for C₂₃H₂₄: C, 92.00; H, 8.00. Found: C, 91.92; H, 8.12.

Hydrogenolysis Followed by Hydrolysis with Deuterium Oxide.—A similar experiment was performed except that the reaction complex was decomposed with 99.4% deuterium oxide. The product obtained was shown by mixed melting point and infrared and nuclear magnetic resonance (n.m.r.) spectra to be identical with that obtained by hydrolysis with ordinary water.

Reaction of Lithium Aluminum Hydride and 7H-Benz[de]anthracene-7-one.—Following the procedure described for the hydrogenolysis of 6-hexylbenzanthrone by lithium aluminum hydride, a suspension of 23.0 g. of benzanthrone⁹ (0.10 mole) in 0.5 l. of dry ether was added to an ether solution (0.5 l.) of lithium aluminum hydride (7.6 g., 0.20 mole, 95+%, Metal Hydrides, Inc.). The solution was refluxed for 18.0 hours. After hydrolysis and purification as described above, benzanthrone was recovered (16.9 g., 73.5%). The residue (5.2 g., 22.6%) obtained upon evaporation of the mother liquor solvent to dryness had an infrared spectrum which contained both carbonyl and hydroxyl absorptions.

Preparation of 7,7-Dideuterio-6-hexyl-7H-benz[de]anthracene.—A solution of lithium aluminum deuteride (1.01 g., 0.0240 mole, Metal Hydrides, Inc., 99.2%) in anhydrous diethyl ether was refluxed for 12.5 hours with 6-hexylbenzanthrone (3.70 g., 0.0118 mole). After the usual work-up, the yield of 7,7-dideuterio-6-hexylbenzanthrene was 71.6% (2.55 g., m.p. 85–87°). A mixed melting point with 6-hexylbenzanthrene was undepressed.

Nuclear Magnetic Resonance Spectra.—Proton nuclear magnetic resonance (n.m.r.) spectra were obtained in carbon tetrachloride solution using a Varian Associates high resolution spectrometer (V-4300 B) operating at 40 megacycles.

An n.m.r. spectrum of 6-hexylbenzanthrone has a complex aromatic hydrogen absorption and a typical aliphatic hydrogen absorption. A comparison of this spectrum with that for propylbenzene shows good correspondence. The n.m.r. spectrum of 6-hexylbenzanthrene has an additional

(12) Compares favorably with ultraviolet data published recently on 6-methylbenzanthrene; ref. 4.

resonance absorption at $+92.8 \pm 1.0$ c.p.s. from an external reference of benzene. This absorption is due to the methylene hydrogen atoms at C-7.

An n.m.r. spectrum of 7,7-dideuterio-6-hexylbenzantrone was identical with the spectrum of 6-hexylbenzantrone but differed from the spectrum of 7,7-dihydro-6-hexylbenzantrone in that the C-7 methylene absorption at $+92.8$ c.p.s. was completely absent. This observation is in accord with the presence of two deuterium atoms at C-7.

Rate Studies on the Conversion of 6-Hexylbenzantrone to 6-Hexylbenzanthrene.—A standard solution of lithium aluminum hydride in ether was prepared (540 ml., 0.422 *N*). Eight independent reductions were run using this solution as follows. Fifty ml. of an ether solution of 6-hexylbenzantrone (0.10 *M*) was added rapidly (<3 sec.) to 50.0 ml. of the standard lithium aluminum hydride solution at reflux. The addition was carried out under dry nitrogen pressure. After the desired time, the reaction was quenched rapidly with water. The products were worked-up as described earlier with the exception that the ether solvent was replaced by carbon tetrachloride for infrared analyses. Results from a typical experiment are shown in Table I.

TABLE I

Reacn. time, min.	Unreacted 6-hexylbenzantrone, %	6-Hexylbenzanthrene, %	Reacn. time, min.	Unreacted 6-hexylbenzantrone, %	6-Hexylbenzanthrene, %
1.0	29.0	..	15.0	29.0	67.5
3.0	26.8	39.0	21.0	26.8	65.0
5.0	30.0	45.0	30.0	27.4	66.0
10.0	25.0	53.0	120.0	27.3	69.0

Infrared analyses were performed in a 0.1-mm. cell in a Perkin-Elmer model 21 double beam recording spectrometer. Graphs of ketone concentration (0.05 *M* – 0.12 *M*) and hydrocarbon concentration (0.08 *M* – 0.40 *M*) versus percentage transmission were linear. Analyses of known mixtures of ketone and hydrocarbon were accurate to 3.0 and 10%, respectively.

Results

6-Hexylbenzantrone was hydrogenolyzed to 6-hexylbenzanthrene by lithium aluminum hydride. Although the mole ratio of lithium aluminum hydride to ketone was varied from 1:1 to 3.8:1 and the reaction time from 2.0 to 20.0 hours, the yields of 6-hexylbenzanthrene and unreacted ketone were always $73 \pm 3\%$ and $15 \pm 3\%$, respectively.

Hydrogenolysis by lithium aluminum hydride followed by hydrolysis with deuterium oxide yielded a product which contained no deuterium. In contrast, hydrogenolysis with lithium aluminum deuteride followed by hydrolysis with water yielded hydrocarbon containing two deuterium atoms at carbon atom seven.

Rate studies indicated that 6-hexylbenzantrone was consumed very rapidly (<1.0 minute). The hydrocarbon formed more slowly.

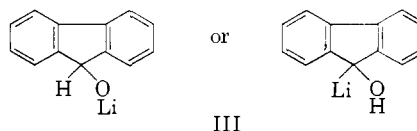
Although an intermediate or side product containing an hydroxyl or ether function was searched for carefully, none could be found.

Infrared spectra of reactions quenched at a series of times from 1.0 to 30.0 minutes indicated that after 1.0 minute, $73.0 \pm 3\%$ of the ketone had been consumed. At this time the concentration of hydrocarbon was too low for analysis by infrared. After 3 minutes the spectra indicated the formation of 39% hydrocarbon which increased linearly to 69% during the next 12 minutes. Spectra at later times indicated no further increase in the yield of hydrocarbon. The yield of hydro-

carbon actually isolated after 15 minutes of reaction was 40%, not 68% as indicated by the infrared spectra.

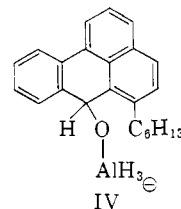
Discussion¹³

Early work in lithium aluminum hydride promoted hydrogenolyses of unsaturated aliphatic carbonyl compounds indicated the presence of carbon-metal bonds in the reaction complex.¹⁴ Later, Bergmann, *et al.*, studied the hydrogenolysis of fluorenone by lithium aluminum hydride and suggested that a stable intermediate (*e.g.*, III) having a carbon metal bond was involved.¹⁵



However, such an intermediate cannot occur in the hydrogenolysis of 6-hexylbenzantrone. The absence of deuterium in the 6-hexylbenzanthrene formed when the reaction complex is decomposed with deuterium oxide and the presence of two deuterium atoms at carbon atom seven when hydrogenolysis is accomplished using lithium aluminum deuteride demonstrate unequivocally that if such an intermediate is formed, it is rapidly and irreversibly converted to a substance which contains no carbon-metal bonds.

The data from this study also exclude an intermediate formed by coordination of aluminum hydride with the carbonyl oxygen atom followed by hydride transfer. Carbon-oxygen bond breaking must proceed simultaneously with hydride transfer for there is no evidence for an intermediate like IV, which could serve as a precursor



to an alcohol. This fact, in conjunction with the rapid disappearance of the carbonyl function, shows that as hydride is transferred, the carbon-oxygen bond fission is completed.

A mechanism which appears to rationalize the difference in the course of the reaction of benzantrone and 6-hexylbenzantrone with lithium aluminum hydride is shown in Fig. 1. Upon treatment of I with lithium aluminum hydride, intermediates V and/or VI form.

The relatively low order of reactivity of the carbonyl grouping in benzantrone¹⁶⁻¹⁸ suggests

(13) An excellent review of lithium aluminum hydride promoted hydrogenolyses appears in "Reduction with Complex Metal Hydrides," N. G. Gaylord, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 979-991.

(14) F. A. Hochstein and W. G. Brown, *THIS JOURNAL*, **70**, 3483 (1948).

(15) E. D. Bergmann, G. Berthier, D. Ginsburg, Y. Hirshberg, D. Lavie, S. Pinchas, B. Pullman and A. Pullman, *Bull. soc. chim. France*, [5] **18**, 661 (1951).

(16) N. Campbell and A. A. Woodham, *J. Chem. Soc.*, 843 (1952).

(17) H. Rule, *et al.*, *ibid.*, 1816 (1950).

(18) J. A. Dixon and H. E. Zieger, unpublished results.

that the carbon-oxygen bond is not readily polarized. If this is true, little hydride ion transfer to carbon atom 7 will take place and upon hydrolysis, benzanthrone will be regenerated (75–85%). The presence of hydroxyl absorption in the infrared spectrum of the crude reduction product does suggest that a small amount of hydride transfer occurs. Then hydrolysis converts V to VII and oxidation by a spontaneous oxidative disproportionation¹⁹ yields ketone Ia and hydrocarbon IIa in equal amounts. The negligible yield of hydrocarbon indicates this must be a minor reaction path.

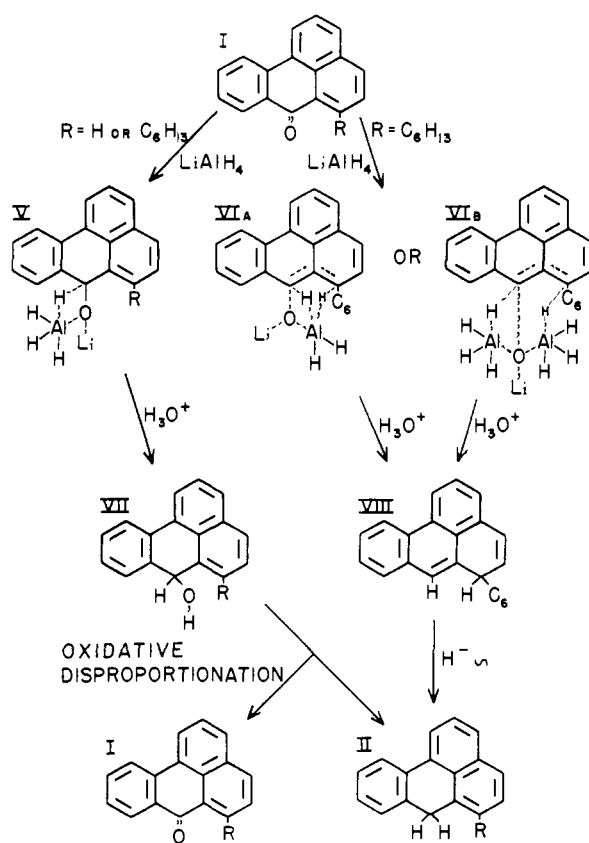


Fig. 1.

In contrast, when R = *n*-alkyl, the inductive effect of the alkyl group promotes electron release from the aromatic ring to the carbonyl carbon. This increases significantly the polarization of the carbon-oxygen bond. Hydride attack at carbon 6 or simultaneous attack at carbons 6 and 7 to yield VIa or VIb ensues.

6-Hexylbenzanthrone has an ideal arrangement of atoms for a 1–4 hydride transfer^{20,21} from the tetrahydroaluminate anion to carbon atom 6 with simultaneous coordination of the aluminum atom with the carbonyl oxygen atom.²² Then,

(19) P. D. Bartlett and J. D. McCollum, *THIS JOURNAL*, **78**, 1441 (1956).

(20) R. E. Lutz and J. S. Gillespie, Jr., *ibid.*, **72**, 2002 (1950).

(21) N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, *ibid.*, **75**, 2283 (1953).

(22) The distance between C-6 and C-7 is estimated at 2.5 ± 0.1 Å., using data published recently on benzanthrone.²³ Since the alumi-

a possible reaction path would involve a double hydride transfer to the 6-hexylbenzanthrone nucleus with concerted carbon-oxygen bond scission. With impending oxygen-aluminum bond formation, one hydride could be transferred to C-7 (four-centered complex) while the other could be transferred to C-6 (cyclic six-membered ring complex) as the aromatic ring electrons facilitate the breaking of the carbon-oxygen σ -bond.²⁵ This would form 6-hexyl-6H-benzanthrene (VIII). A subsequent 1–3 hydride shift may account for the conversion of 6H- to 7H-isomer (VIII-IIb). A recent and detailed study of the isomeric benzanthrenes has shown that 6-methyl-6H-benzanthrene isomerizes readily to 6-methyl-7H-benzanthrene.⁹

If both hydrides transferred have a common origin (VIa), the leaving group would be LiOAlH_2 . Certainly, a simultaneous attack at C-7 by two hydride ions appears less likely than initial, but simultaneous, hydride transfer at different carbon centers.

If, hydride ion attack occurs first at carbon atom 7 to yield V, a partial positive charge is not obtained on carbon atom 6 and the reaction may proceed to VII. Oxidation of VII as noted above would yield 6-hexylbenzanthrone (Ib) and 6-hexylbenzanthrone (II). However, since no trace of VII could be found and no evidence for the hydroxyl group was observed in the infrared spectra it appears that, as with benzanthrone, the complex V is stable and on hydrolysis 6-hexylbenzanthrone (Ib) is recovered.

Nystrom and Berger have shown that aromatic carbonyl compounds are hydrogenolyzed with mixtures of aluminum chloride and lithium aluminum hydride.²⁶ Further, an alicyclic ketone having a conjugated double bond²⁷ and benzanthrone²⁸ have been hydrogenolyzed with this mixed reagent. However, as shown in the present work, the Lewis acid is not necessary for the hydrogenolysis of the 6-alkylbenzanthrone. It appears that all these observations may be rationalized as follows: (1) aluminum chloride is a far stronger Lewis acid than aluminum hydride and through coordination with the carbonyl oxygen causes greater carbon-oxygen bond weakening in benzanthrone than aluminum hydride does; this, we believe, is the principal function of the aluminum chloride in aiding lithium aluminum hydride-aluminum chloride promoted hydrogenolyses; (2) LiOAlCl_3^- should be a better leaving group than LiOAlH_3^- ; (3) in 6-hexylbenzanthrone the alkyl group at carbon atom six exerts a static

num-hydrogen bond distance²⁴ is 1.64 Å. and the carbonyl bond distance is 1.19 Å., the distance between C-6 and the carbonyl oxygen atom is about 1.41 Å., well within reaction range for a hydride transfer at C-6.

(23) T. H. Goodwin, *J. Chem. Soc.*, 1689 (1955).

(24) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 168, 179.

(25) Gaylord (ref. 14, p. 981) has likened hydrogenolysis of fluorenone to the hydrogenolysis of amides wherein the α,β -double bond performs the same function as the unshared electrons on nitrogen in aiding the cleavage of the carbon-oxygen bond.

(26) R. F. Nystrom and C. R. A. Berger, *THIS JOURNAL*, **80**, 2896 (1958).

(27) J. Broome and B. R. Brown, *Chemistry & Industry*, 1307 (1956); O. H. Wheeler and J. C. Mateos, *ibid.*, 395 (1957).

(28) B. R. Brown and A. M. S. White, *J. Chem. Soc.*, 3755 (1957).

inductive effect. The net effect is the resonance stabilization of a partial positive charge on carbon atoms 7 and 6 and a weakening of the carbon-oxygen bond during reduction. The result is hydrogenolysis.

Acknowledgment.—The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible and to Mr. William B. Moniz, who obtained and interpreted the nuclear magnetic resonance spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

4-Deoxy-3-oxo-D-glycero-2-hexulose, the Dicarbonyl Intermediate in the Formation of D-Isosaccharinic Acids¹

BY ROY L. WHISTLER AND J. N. BEMILLER

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An intermediate in the formation of D-isosaccharinic acids is isolated. Evidence that the isolated compound is 4-deoxy-3-oxo-D-glycero-2-hexulose is given by its oxidation to glycolic acid and 2-deoxy-D-glycero-tetronic acid and by the formation of the typical α -dioxo color reaction.

Knowledge of the mechanism by which saccharinic acids are produced through alkaline rearrangement of sugars has accumulated gradually over a period of time. Saccharinic acid formation by recombination of sugar fragments was discussed by Kiliani² and Windaus.³ Nef⁴ made the first extensive proposal of a reaction mechanism by suggesting an isomerization of sugar enediols and epoxy compounds to an α -dicarbonyl compound which would undergo a benzylic acid type of rearrangement to a saccharinic acid. Evans and co-workers⁵ suggested that the initial isomerization might be effected through unsaturated oxide compounds but believed as others that the final step was a rearrangement of an α -dicarbonyl compound. Isbell⁶ put the mechanism on a modern basis and showed that the α -dicarbonyl compound could be formed by consecutive electron-displacement reactions. Kenner and co-workers⁷ demonstrated that the position of substitution on a sugar unit determined the acid which would be formed and that 4-O-substitution^{7b} resulted in the formation of isosaccharinic acid through elimination of the substituent group as an alkoxy or glycosyloxy anion. This refinement of Isbell's proposal has been popularly known as the β -alkoxy carbonyl mechanism because elimination required a carbonyl group in the β -position to an etheric or glycosidic linkage. When a 4-O-substituted sugar is dissolved in an alkaline solution, this positioning occurs through a preliminary Lobry de Bruyn-Alberda van Ekenstein isomerization.⁸

Blears, Machell and Richards⁹ obtained evidence of an intermediate in D-isosaccharinic acid formation by the appearance of a new spot on paper chromatography

when 4-O-substituted-D-glucose derivatives were degraded in 0.05 N sodium hydroxide solutions instead of lime water. This compound was removed from the reaction mixture by formation of the insoluble bis-2,4-dinitrophenylhydrazone (m.p. 249°). They suggested that it was the postulated dicarbonyl intermediate.

Two of these same authors have obtained indirect evidence for the formation of the dicarbonyl compound during the alkaline degradation of 4-O-substituted-D-glucose units by the detection of glycoaldehyde,⁹ 2-deoxy-D-glycero-tetrose⁹ and glycolic and 2-deoxy-tetronic acids¹⁰ after the action of dilute sodium hydroxide solutions, both at boiling and room temperatures. It is suggested by these authors⁹ that glycolic and 2-deoxy-D-tetronic acids are formed by an alkaline cleavage of the α -dicarbonyl system similar to that observed with benzil when the benzylic acid rearrangement is inhibited.¹¹

In continuation of work in this Laboratory on the alkaline degradation of polysaccharides, a substance is now isolated from cellobiose (I) after the action of oxygen-free potassium hydroxide solution, which apparently is an intermediate in the formation of D-isosaccharinic acids and has properties leading us to believe it is the dicarbonyl compound, 4-deoxy-3-oxo-D-glycero-2-hexulose (II).^{11a} Isolation of this compound is accomplished after stopping isomerization by neutralization. If lime water is used as the alkaline solution, the benzylic acid type of rearrangement to D-isosaccharinic acids occurs so rapidly that no intermediate can be isolated.

The combined information presented here gives support to the generally accepted belief that calcium ions specifically catalyze the formation of

(1) Journal Paper No. 1528 of the Purdue Agricultural Experiment Station.

(2) H. Kiliani and S. Kleemann, *Ber.*, **17**, 1302 (1884).

(3) A. Windaus, *Chem. Ztg.*, **29**, 564 (1905).

(4) J. U. Nef, *Ann.*, **357**, 214 (1907); **376**, 1 (1910).

(5) W. L. Evans, R. H. Edgar and G. P. Hoff, *THIS JOURNAL*, **48**, 2665 (1926).

(6) H. S. Isbell, *J. Research Natl. Bur. Standards*, **32**, 45 (1944).

(7) (a) W. M. Corbett and J. Kenner, *J. Chem. Soc.*, 2245 (1953);

(b) J. Kenner and G. N. Richards, *ibid.*, 278 (1954).

(8) C. A. Lobry de Bruyn and W. Alberda van Ekenstein, *Rec. Trav. chim.*, **14**, 203 (1895); **16**, 262 (1897).

(9) M. J. Blears, G. Machell and G. N. Richards, *Chemistry & Industry*, 1150 (1957).

(10) G. Machell, G. N. Richards and H. H. Sephton, *ibid.*, 467 (1957); G. N. Richards and H. H. Sephton, *J. Chem. Soc.*, 4492 (1957); G. Machell and G. N. Richards, *ibid.*, 1199 (1958).

(11) E. Pfeil, G. Geissler, W. Jacquemin and F. Lömker, *Ber.*, **89**, 1210 (1956).

(11a) Since this paper was submitted for publication, E. F. L. J. Anet, *THIS JOURNAL*, **82**, 1502 (1960), has reported briefly the isolation of 3-deoxy-D-erythro-hexosone (3-deoxy-2-oxo-D-erythro-hexose), the dicarbonyl intermediate in the formation of D-glucometasaccharinic acids, and 3-deoxy-D-threo-hexosone (3-deoxy-2-oxo-D-threo-hexose), the dicarbonyl intermediate in the formation of D-galactometasaccharinic acids. The rapid conversion of each by lime water to the corresponding saccharinic acids further substantiates the accepted mechanism.