[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Synthesis and Oxidation of Polymethylene Bis-cycloalkenes[1]

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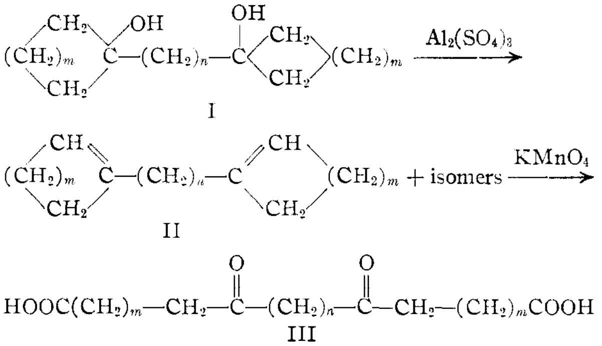
Olefins derived from the dehydration of diglycols from the reaction of di-Grignard reagents with a cycloalkanone have been prepared. Evidence for their structure was obtained by oxidation to the corresponding aliphatic diketodicarboxylic acids. Only acids derived from diolefins with the double bond contained in the ring (II) could be isolated. A product, IV, obtained from a mono-adduct of cyclohexanone also was isolated.

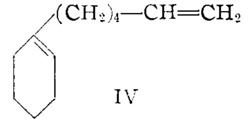
In the course of work on the preparation of higher aliphatic α,ω-dicarboxylic acids, several approaches were investigated.[2]

The method to be described in this paper involves the reaction between an α,ω-di-Grignard reagent[2] and a cycloalkanone. The polymethylene-*bis*-*t*-cycloalkanol formed (I) was not isolated but subsequently dehydrated to yield a polymethylene-bis-cycloalkene; oxidation of the cycloalkene by treatment with potassium permanganate gave an aliphatic diketodicarboxylic acid. Although only one dicarboxylic acid was isolated from the oxidation reactions, it is possible that isomeric olefins having the same boiling point may also be present in smaller quantities. The degree to which a double bond prefers the exocyclic or endocyclic position may be a function of the ring size.



$$HOOC(CH_2)_m—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—(CH_2)_n—\overset{\overset{\displaystyle O}{\|}}{C}—CH_2—(CH_2)_mCOOH$$

When $m = 3$, $n = 6$, I was not isolated but was converted directly to the diene in 23.4% yield, identified by oxidation to 6,13-diketoöctadecane-1,18-dioic acid III, $m = 3$, $n = 6$. A mixed melting point with a known sample was not depressed.[2] A major side reaction was the reduction of the cyclohexanone by either the mono-adduct of the di-Grignard reagent or the di-Grignard reagent itself. Thus, cyclohexanol (10.5%) and IV (29.7%) were also obtained as reaction products. Cyclohexanol was identified as the cyclohexyl N-phenylcarbamate. Evidence for the structure of IV was



IV

obtained by oxidation to the corresponding keto dibasic acid, a known compound.[3,4] Optimum yields of II were obtained by using stoichiometric amounts of the reactants in ether.

When $m = 2$, $n = 6$, a 12.1% yield of II was obtained. Evidence for its structure was obtained by oxidation to give the known 5,12-diketohexadecane-1,16-dioic acid.[2,5] A mixed melting point with an authentic sample was not depressed.

When $m = 3$, $n = 10$, II was isolated in 11.8% yield, tentatively identified by analysis only.

Experimental[6]

1,6-Bis-(1-cyclohexen-1-yl)-hexane, II ($m = 3$, $n = 6$).—A mixture of 61 g. (0.25 mole) of 1,6-dibromohexane, 12.2 g. (0.5 g. atom) of powdered magnesium, a small crystal of iodine, and 210 ml. of anhydrous ether was refluxed gently for three hours after the initial vigorous reaction abated. For titration data see ref. 2. Cyclohexanone (49 g., 0.5 mole) was added slowly, keeping the temperature at 5–10°. The mixture was refluxed for one hour, cooled and decomposed by pouring into 400 ml. of a 20% aqueous solution of ammonium chloride. The ether layer was separated, washed twice with 100 ml. of a saturated (40%) aqueous solution of sodium bisulfite, filtered, washed twice with 200 ml. of water, dried over potassium carbonate and evaporated by distillation, yielding 55–59 g. of residue. To ensure the complete dehydration of this crude alcohol mixture it was necessary to distil the mixture from anhydrous aluminum sulfate.

A 100-ml., single-necked, round-bottomed flask containing 5 g. of anhydrous aluminum sulfate was fitted with a Claisen head and receiving flask and immersed in a Wood's metal bath at 300–320°. The alcohol mixture was added dropwise. The lower distillate layer consisting of water was removed and discarded. The aluminum sulfate was cooled and extracted with 100 ml. of ether. The liquid product and ether were combined, dried over calcium chloride and fractionated through a 40-cm. Podbielniak column. Two separate fractions were obtained. On refractionation, the first gave 12.2 g. (29.7%) of IV, b.p. 78–80° (4 mm.), $n^{25}D$ 1.4700. IV on reduction over platinum absorbed 94.7% of the theoretical amount of hydrogen.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27; mol. wt., 164.3. Found: C, 87.53; H, 12.61; mol. wt., 158.5, 157.4 (cryoscopic, benzene).

The second fraction gave 14.4 g. (23.4%) of II ($m = 3$, $n = 6$), b.p. 166–168° (4 mm.), $n^{25}D$ 1.4951.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.80; H, 12.20; mol. wt., 246.4. Found: C, 87.60; H, 12.17; mol. wt., 236.4 (cryoscopic, benzene).

If the crude mixture of alcohols from above was distilled directly, partial spontaneous dehydration occurred, but it was possible to obtain cyclohexanol in addition to IV and II ($m = 3$, $n = 6$). The low boiling fraction was treated with 20 ml. of saturated aqueous sodium bisulfite to remove unreacted cyclohexanone and refractionated. The fraction boiling at 159–160° (atm.) was collected, 5.23 g. (10.5%), $n^{25}D$ 1.4581; reported for cyclohexanol 160.9–161.0° (760 mm.),[7] $n^{25}D$ 1.4642.[8] A small portion was converted to cyclohexyl N-phenylcarbamate by treatment with

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[1] Taken from the thesis of A. Kreuchunas, submitted in partial fulfillment of the requirements for the Ph.D. degree at the Massachusetts Institute of Technology, June, 1950.

(2) A. Kreuchunas, THIS JOURNAL, **75**, 3339 (1953).

(3) J. C. Sauer, *ibid.*, **69**, 2444 (1947).

(4) J. English, Jr., *ibid.*, **63**, 941 (1941).

(5) H. Lettré and A. Jahn, *Ber.*, **85**, 346 (1952).

(6) All melting points are corrected.

(7) K. K. Kelley, THIS JOURNAL, **51**, 1400 (1929).

(8) C. S. Hiers and R. Adams, *ibid.*, **48**, 2385 (1926).

phenyl isocyanate,[9] m.p. 85–86°, after recrystallization twice from petroleum ether. A known sample of cyclohexanol was similarly converted, m.p. 82–84°, mixed m.p. 82–84.5°.

6-(1-Hydroxycyclohexyl)-hexene-1.—By omitting the sodium bisulfite wash during the isolation of the crude alcohol mixture above, spontaneous dehydration was minimized, and it was possible to isolate two high boiling compounds. The first was a colorless liquid which weighed 15 g., b.p. 86° (0.125 mm.), n^{25}D 1.4774. It was tentatively identified as 6-(1-hydroxycyclohexyl)-hexene-1.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.05; H, 12.16. Found: C, 78.96; H, 12.19.

The second compound was a thick, colorless oil which slowly crystallized and which weighed 8.0 g., b.p. 125° (0.10 mm.). The crystalline material was recrystallized from ethyl acetate, then from ether, m.p. 97.5–99°. This compound has not been identified.

Anal. Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.49, 73.56; H, 12.24, 11.95.

6-Ketoundecane-1,11-dioic Acid.—A mixture of 3.28 g. (0.02 mole) of IV, 40 ml. of acetone and 4 ml. of water was cooled in an ice-bath. Potassium permanganate (13.0 g., 0.85 mole) which had been previously ground to a fine powder was added to the stirred mixture over a period of four hours. The thick, brown paste was washed into a beaker with 100 ml. of water and treated with small portions of sodium bisulfite and concentrated hydrochloric acid until the solution cleared. A small amount (0.2 g.) of colorless solid was removed by filtration, m.p. 93–113°. The filtrate was extracted with two 150-ml. portions of ether and the ether was removed by evaporation. The solid residue (0.5 g. (11%), m.p. 109–114°) which remained was recrystallized twice from a mixture of chloroform and petroleum ether and twice from benzene, m.p. 113.2–113.8°; reported for 6-ketoundecane-1,11-dioic acid, m.p. 109°[3] and 111°.[4]

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88; neut. equiv., 115.1. Found: C, 57.63; H, 8.12; neut. equiv., 114.3.

6,13-Diketoöctadecane-1,18-dioic Acid, III (*m* = 3, *n* = 6).—II (*m* = 3, *n* = 6) (4.97 g., 0.02 mole) was oxidized in the same manner as described for IV and yielded 1.77 g. (25.8%) of a colorless solid, m.p. 125–131°. The product was recrystallized once from water, dried and digested with chloroform, m.p. 135–136°. An authentic sample of III (*m* = 3, *n* = 6),[2] m.p. 134–135°, was mixed with a portion of the product, mixed m.p. 136–137.5°.

1,6-Bis-(1-cyclopenten-1-yl)-hexane, II (*m* = 2, *n* = 6).—This compound was prepared in the same manner as described for II (*m* = 3, *n* = 6). Cyclopentanone (84 g., 1.0 mole, twice theoretical amount) was used as the ketone component. The crude mixture of alcohols was distilled, and the fraction boiling from 120–180° (4 mm.), (37.2 g.) was dehydrated over aluminum sulfate.

The crude product obtained after dehydration was fractionated through a 40-cm. Podbielniak column. II (*m* = 2, *n* = 6) was collected at 143–146° (4 mm), 6.6 g., n^{25}D 1.4980, 12.1% over-all yield.

Anal. Calcd. for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 87.61; H, 11.67.

5,12-Diketohexadecane-1,16-dioic Acid, III (*m* = 2, *n* = 6).—II (*m* = 2, *n* = 6) (2.18 g., 0.01 mole) was oxidized in the same manner as described for IV. A colorless solid was obtained which weighed 1.5 g., m.p. 130–136°, 47.7%. The compound was recrystallized from water, methanol, ligroin and acetic acid, m.p. 142.2–143.4°; reported for III (*m* = 2, *n* = 6), m.p. 141–141.5°.[5] An authentic sample, m.p. 141.4–142.6°,[2] was mixed with a portion of product. The mixed m.p. was 141.2–142.6°.

1,10-Bis-(1-cyclohexen-1-yl)-decane, II (*m* = 3, *n* = 10).—This compound was prepared in the same manner as described for II (*m* = 3, *n* = 6). The di-Grignard reagent was prepared from 75.0 g. (0.25 mole) of 1,10-dibromodecane.[2] The crude mixture of alcohols was distilled with the expected partial dehydration, and the fraction boiling from 185–215° (4 mm.) (18.1 g.) was dehydrated over aluminum sulfate.

The crude product obtained after dehydration was fractionated through a 40-cm. Podbielniak column. Two fractions were collected: 2.5 g., b.p. 187–195° (2 mm.), n^{25}D 1.4900; 6.4 g., b.p. 195–198° (2 mm.), n^{25}D 1.4909. The over-all yield of II (*m* = 3, *n* = 10), based on these two fractions, was 11.8%.

Anal. Calcd. for $C_{22}H_{38}$: C, 87.34; H, 12.66. Found: C, 87.04; H, 12.65.

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[9] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 226.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GLIDDEN COMPANY—NAVAL STORES DIVISION]

Nopol. IV. Synthesis of 1(7),8-*p*-Menthadiene and 1(7)-*p*-Menthene

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The alcohols, dipentene-7-carbinol and carvomenthene-7-carbinol, slowly decompose at their boiling points with loss of formaldehyde to form 1(7),8-*p*-menthadiene and 1(7)-*p*-menthene, respectively. The reverse reaction, condensation of the hydrocarbons with formaldehyde to form the carbinols, takes place in sealed tubes at 175°.

The condensation of β-pinene (I) and formaldehyde to form the dicyclic alcohol nopol (II) was recently shown to be reversible[1] under the influence of heat though the decomposition of nopol was complicated by its racemization and its simultaneous isomerization to the acyclic alcohol, alloöcimenecarbinol and the monocyclic alcohol, 1,8-*p*-menthadiene-7-carbinol (dipentene-7-carbinol) (III).

It is the purpose of this paper to report that 1,8-*p*-menthadiene-7-carbinol (III) also decomposes slowly near its boiling point at atmospheric pressure, and that there is formed formaldehyde and a hydrocarbon which has been identified as 1(7),8-*p*-menthadiene (pseudo- or ψ-limonene) (IV). Further, its partial reduction product, 1-*p*-menthene-7-carbinol (carvomenthene-7-carbinol) (V), decomposes similarly to yield 1(7)-*p*-menthene (VI). These decompositions are reversible since the hydrocarbons IV and VI may be caused to react with formaldehyde at 175° in sealed tubes to re-form the corresponding alcohols III and V.

The general applicability of this decomposition to the synthesis of compounds of structure $R^1(R^2CH_2)C{=}CH_2$ from carbinols of structure $R^1(R_2CH{=})C{-}CH_2CH_2OH$ and the reverse condensation of the olefin with formaldehyde to yield the carbinol has not yet been studied in a large number of cases, though other work in these laboratories has shown[2] that the reaction is applicable to the de-

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[1] J. P. Bain, A. H. Best and R. L. Webb, THIS JOURNAL, 74, 429 (1952).

[2] Unpublished work.