bulky potassium atom in the 2-position would interfere much more with the free rotation of the methyl group than would a benzyl group. Consequently, entropy considerations would favor addition of the benzyl group to the 2-position, and this is consistent with the experimental data.

With the lithium atom, on the other hand, its relatively small size would permit the formation of a more localized bond in the propylene–lithium ion complex. The positive charge should be concentrated on the secondary carbon atom of such a complex since secondary carbonium ions are much more stable than primary carbonium ions. The addition of a benzyl anion to the 2-position would consequently have a much lower activation energy than addition to the 1-position, again consistent with the experimental data. The entropy factors should be just opposite to those for a potassium atom and should favor addition of the benzyl group to the 1-position, as the data indicate. The sodium atom, which is intermediate in size, is also intermediate with respect to energy and entropy of activation.

An alternative explanation for the increase in n-butylbenzene formation at higher temperatures with the sodium and lithium catalysts could be the occurrence of some side chain alkylation through a free radical intermediate. The present data do not provide the basis for a definite choice between these two possibilities.

Acknowledgment.—The authors wish to thank Professor Richard Powell for his helpful discussions on the problem and to acknowledge the assistance of Dr. R. D. Vanselow in obtaining some of the data.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, NEW YORK 20, N. Y.]

Pyrolysis of β-Hydroxyolefins. III. A Novel Method for Extending Carbon Chains

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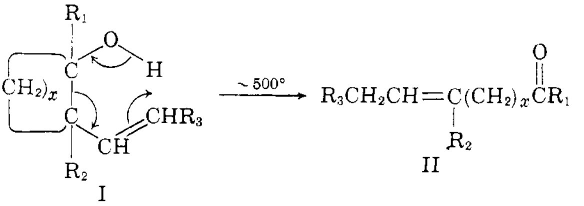
RECEIVED FEBRUARY 11, 1960

A new method is described for extending carbon chains. It is based upon the synthesis of 2-(1'-alkenyl)-cycloalkanols which, when pyrolyzed at temperatures near 500°, yield long open-chain, unsaturated, carbonyl compounds.

In two earlier publications[4,5] from this Laboratory, it has been demonstrated that the pyrolysis of β-hydroxyolefins to give olefinic substances and carbonyl compounds is a general reaction, and the evidence[5] strongly supports the view that this transformation proceeds *via* a cyclic transition state.

As previously employed, the thermal decomposition of β-hydroxyolefins is a degradation reaction leading to the formation of two distinct molecular species. It occurred to us, however, that if the carbon–carbon bond undergoing fission were made an appropriate element of a cyclic structure, the reaction could be employed as a new and general method for extending carbon chains as indicated.

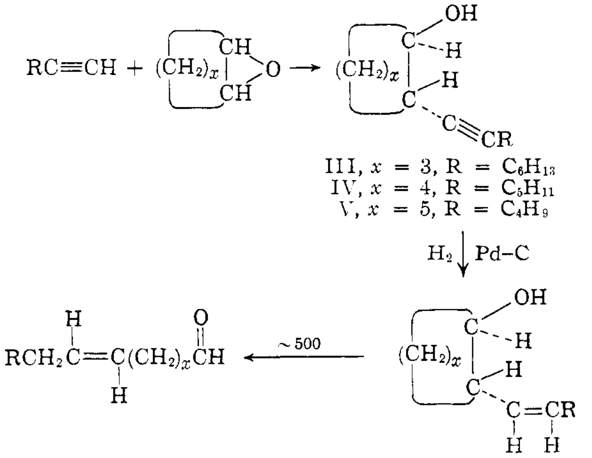


I

II

If the proposed mechanism[5] is valid, one should be able to predetermine the exact location of the carbon–carbon double bond with respect to the carbonyl group by merely selecting a proper value for "x" in I, since it has been established that[4] the newly formed olefinic bond is not prone to rearrange under the experimental conditions employed.

The above expectations have now been fully realized. In this preliminary paper, we wish to report on three specific examples in which carbon chains have been extended by five, six and seven carbon atoms to yield isomeric unsaturated aldehydes containing thirteen carbon atoms. The major reaction sequence is outlined.



III, $x = 3$, R = C_6H_{13}
IV, $x = 4$, R = C_5H_{11}
V, $x = 5$, R = C_4H_9

VI, $x = 3$, R = C_6H_{13}
VII, $x = 4$, R = C_5H_{11}
VIII, $x = 5$, R = C_4H_9

IX, $x = 3$, R = C_6H_{13}
X, $x = 4$, R = C_5H_{11}
XI, $x = 5$, R = C_4H_9

Although monosubstituted or asymmetrically disubstituted ethylene oxides react readily with lithium acetylides to form open-chain acetylenic alcohols,[4,6] we have found the oxides of cyclic olefins to be relatively inert toward these reagents. In fact, when ether was used as solvent, no appreciable amount of product was formed. Even when boiling dioxane was employed as a solvent, we were able to

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obtain III, IV and V in yields of only 12, 40 and 30%, respectively, after a period of several hours. Our observations are essentially in accord with those reported by Inhoffen and co-workers[7] who found the reaction of cyclohexene oxide with lithium acetylides to be particularly sluggish. These authors claim substantially higher reaction rates and product yields, however, when ammonia at elevated temperatures was employed as solvent.

Alkenyllithium compounds are more powerful as nucleophilic reagents than are lithium acetylides and react with ethylene oxides to give β-hydroxyolefins[4] directly. Unfortunately, the appropriate vinyl halides required for the preparation of these reagents are often not conveniently available. A case in point is the *trans* isomer of VI which we have obtained in a yield of 33% by allowing cyclopentene oxide to react with the alkenyllithium formed from 1-bromo-1-octene. The *trans* configuration assigned to the product of this reaction on the basis of its infrared spectrum was anticipated in view of the experimental conditions employed.[8,9]

Partial catalytic hydrogenation of the acetylenic alcohols III, IV and V proceeded in a highly satisfactory manner to give high yields of the *cis*-β-hydroxyolefins VI, VII and VIII. The latter compounds when passed through a heated tube (500°) underwent a smooth rearrangement to produce the isomeric tridecenals IX, X and XI, respectively, in yields of at least 55–60%.

The homogeneity of the unsaturated aldehydes was strongly indicated by the fact that each readily formed a characteristic 2,4-dinitrophenylhydrazone. This further substantiates our belief[4] that the newly formed carbon–carbon double bond is not prone to migrate during the course of the experiment. Oxidative degradation of IX, X and XI confirmed the location assigned to the double bond. As anticipated, the unsaturated aldehydes gave similar but different infrared absorption spectra with strong bands at the expected locations [*i.e.*, 3.8 μ (aldehyde C—H), 5.85 μ (—C(H)=O), 6.88 and 10.3 μ (*trans* —CH=CH—)].

Although the mechanism which has been proposed[4] for the pyrolysis of β-hydroxyolefins does not allow us to predict with accuracy the configuration about the newly formed olefinic double bond, the strong adsorption band at 10.3 μ leaves little doubt[10] that compounds IX, X and XI possess *trans* configurations.

Owing to the linear geometry associated with acetylenic compounds and the resultant difficulties attending the formation of cyclic transition states involving the hydroxyl group, it was assumed that the acetylenic alcohols III, IV and V would not undergo facile pyrolysis to give unsaturated aldehydes. This view is supported experimentally. When IV was subjected to pyrolysis, under the same experimental conditions as those employed with the β-hydroxyolefins, there was obtained a complex mixture containing only a small amount (*i.e.*, about 15%) of aldehydic material. Approximately 42–45% of the acetylenic alcohol IV was recovered.

In a subsequent paper, it will be shown that this new method for extending carbon chains may be used very effectively for the synthesis of long-chain unsaturated ketones.

Experimental

***trans*-2-(1'-Octynyl)-cyclopentanol-(III).**—To a stirred solution of 1-octyne (55 g.) in purified, dry dioxane (750 ml.) was added dropwise an ethereal solution of butyllithium (290 ml., 1.55 *M*). The reaction was carried out in an inert atmosphere (nitrogen). The resulting mixture was boiled for 1 hour, and to this was added cyclopentene oxide (39 g.), and heating under reflux was continued for 40 hours. The excess dioxane was removed by distillation and the residue decomposed with ice and acetic acid (30 ml.). The mixture was extracted with ether and the latter solution dried (Na_2SO_4) and fractionated. The fraction boiling at 100–130° (1 mm.) was refractionated to give 2-(1'-octynyl)-cyclopentanol (10.6 g., 12%), b.p. 144° (5 mm.), $n^{25}D$ 1.4774.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 79.8; H, 11.4.

***trans*-2-(1'-Heptynyl)-cyclohexanol (IV)** was prepared by the general method described above. The lithium salt of 1-heptyne (38.4 g.) was prepared by allowing the hydrocarbon to react with an ethereal solution of butyllithium (315 ml., 1.25 *M*). The lithium acetylide derivative was allowed to react with cyclohexene oxide (40 g.) in dry dioxane (600 ml.) for 19 hours at the boiling point of the solution. After decomposition of the mixture (as described in the earlier example) there was obtained 2-(1'-heptynyl)-cyclohexanol; yield 32 g. (41%), b.p. 131° (7 mm.), $n^{25}D$ 1.4801.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.4; H, 11.3.

***trans*-2-(1'-Hexynyl)-cycloheptanol (V)** was obtained by the general procedure as described above by allowing the lithium salt from 1-hexyne (24.6 g.) to react with cycloheptene oxide (29.8 g.) in boiling dioxane (300 ml.) solution for a period of 16 hours. The product—after decomposition of the reaction mixture in the usual way—was obtained by fractionation; yield 15.5 g. (30%), b.p. 141°(7 mm.), $n^{25}D$ 1.4856.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 79.9; H, 11.3.

***trans*-(1'-*cis*-Octenyl)-cyclopentanol (VI)** was prepared by the hydrogenation (3 atm. pressure, 27°) of *trans*-2-(1'-octynyl)-cyclopentanol (14 g.) with Lindlar catalyst (7 g.) in methanol (50 ml.) containing quinoline (1 ml.) according to the procedure of Gensler and Abrahams.[6] Hydrogenation ceased after the absorption of one equivalent of hydrogen. The catalyst was removed by filtration, and the solution was fractionated to give the expected product; yield 12.5 g. (86%), b.p. 139° (12 mm.), $n^{25}D$ 1.4722.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.4; H, 12.2.

***trans*-(1'-*cis*-Heptenyl)-cyclohexanol (VII).**—Hydrogenation (3 atm. pressure, 27°) of *trans*-2-(1'-heptynyl)-cyclohexanol (15 g.) in methanol solution (50 ml.) containing quinoline (1 ml.) with Lindlar catalyst (7 g.) gave the anticipated olefinic alcohol; yield 13.5 g. (90%), b.p. 137° (7 mm.), $n^{25}D$ 1.4733.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.3; H, 12.0.

***trans*-2-(1'-*cis*-Hexenyl)-cycloheptanol (VIII).**—In a manner similiar to that described above for the isomeric compounds, *trans*-2-(1-hexynyl)-cycloheptanol (14.5 g.) was hydrogenated with Lindlar catalyst until one mole of hydrogen was absorbed. After removal of the catalyst by filtration, the product was purified by fractionation; yield 13 g. (89%), b.p. 134° (7 mm.), $n^{25}D$ 1.4796.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.8; H, 12.3.

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[8] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951).

[9] A. S. Dreiding and F. J. Pratt, THIS JOURNAL, **76**, 1902 (1954).

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Preparation of Open-chain Unsaturated Aldehydes. 1. *trans*-**Tridecen-5-al (IX).**—*trans*-2-(1′-*cis*-Octenyl)-cyclopentanol (12 g.) was pyrolyzed by passing it dropwise (30 g./hr.) through a heated (500°) Vycor tube (12″ long, 1″ wide) packed with Pyrex glass helicies and swept with dry nitrogen as an inert atmosphere. The cooled condensate was collected and fractionated to give *trans*-tridecen-5-al; yield 6.6 g. (55%), b.p. 138° (13 mm.), n^{25}D 1.4539.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.7; H, 12.2.

The unsaturated aldehyde was also formed in 55% yield by the thermal isomerization of *trans*-2-(1′-*trans*-octenyl)-cyclopentanol at 500°. Identical 2,4-dinitrophenylhydrazones were formed from each sample; m.p. 96–97°.

Anal. Calcd. for $C_{19}H_{25}N_4O_4$: C, 60.62; H, 7.50; N, 14.88. Found: C, 60.6; H, 7.4; N, 15.0.

2. *trans*-**Tridecen-6-al (X)** was prepared by pyrolyzing *trans*-2-(1′-*cis*-heptenyl)-cyclohexanol (12 g.) at 500° as described above; yield 6.6 g., b.p. 138° (13 mm.), n^{25}D 1.4513.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.6; H, 12.2.

The 2,4-dinitrophenylhydrazone had m.p. 71–72°.

Anal. Calcd. for $C_{19}H_{28}N_4O_4$: C, 60.62; H, 7.50; N, 14.88. Found: C, 60.8; H, 7.6; N, 15.0.

3. *trans*-**Tridecen-7-al (XI).**—Under the same condition as those described above, *trans*-2-(1′-*cis*-hexenyl)-cycloheptanol (12 g.) was rearranged thermally; yield 7.2 g. (60%), b.p. 138° (13 mm.), n^{25}D 1.4580.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.7; H, 11.9.

Although the 2,4-dinitrophenylhydrazone of this aldehyde—like that from IX—had m.p. 96–97°, a mixture of the two samples melted at 93–97°.

Anal. Calcd. for $C_{19}H_{28}N_4O_4$: C, 60.62; H, 7.50; N, 14.88. Found: C, 60.8; H, 7.3; N, 15.1.

trans-**2-(1′-*trans*-Octenyl)-cyclopentanol.**—To a cooled (0°) suspension of lithium (6.9 g.) in dry ether (350 ml.), 1-bromo-1-octene (96 g.) in ether (100 ml.) was added dropwise in an atmosphere of nitrogen. Stirring at low temperature was continued for 3 hours after which cyclopentene oxide (40 g.) was added in one portion, and the mixture was allowed to warm to room temperature. After an additional hour, the mixture was heated to boiling and maintained at that temperature for 20 hours. The cooled mixture was filtered to remove a small quantity of unreacted lithium, and the filtrate was decomposed with ice and acetic acid (30 ml.). The organic compounds were extracted with ether, and the ether phase was washed with carbonate solution, dried and distilled to give the unsaturated alcohol; yield 31 g. (33%), b.p. 130° (6 mm.), n^{25}D 1.4724.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.7; H, 12.4.

The action of this compound on pyrolysis was indistinguishable from that of VI and gave *trans*-tridecen-5-al in a yield of 55%.

Pyrolysis of *trans*-2-(1′-Heptynyl)-cyclohexanol (IV).—This acetylenic alcohol (14.5 g.) was subjected to the same pyrolytic conditions (500°) as used for the corresponding olefinic analog VII. The infrared spectrum of the crude pyrolysate indicated that some aldehyde had formed. A fractionation of this material through a 2′ spinning band column at 10 mm. pressure allowed a partial separation into three fractions: (1) b.p. 58–120°, 1.5 g., 11%; (2) b.p. 126–136°, 1.4 g., 9% (3) b.p. 136–140°, 5.5 g., 38%. Fraction 1 consisted mainly of aldehyde, fraction 2 was composed of aldehyde plus starting yne-ol while 3 was mainly starting material.

Oxidative Degradation of the Isomeric Tridecenals. (a) *trans*-**Tridecen-5-al (IX).**—Ozone was bubbled through a solution of the aldehyde (3 g.) in ethyl acetate (50 ml.) at −80°. The reaction was stopped when an excess of ozone was present, and the ozonide was decomposed by adding dropwise to boiling water (50 ml.). The cooled aqueous mixture was extracted with ethyl acetate, and the organic phase dried over sodium sulfate and evaporated. Oxidation of this crude aldehydic residue was accomplished in acetone solution (30 ml.) at 25° with $KMnO_4$ (1.8 g.). The MnO_2 was filtered, and the filtrate evaporated. After dissolution of the MnO_2 in a saturated bisulfite solution, this aqueous solution was acidified with hydrochloric acid and thoroughly extracted with ether. The residue from evaporation of the ether and that from the acetone filtrate were combined and distributed between petroleum ether–water.

The octanoic acid obtained from the petroleum ether phase was dried by azeotropic distillation from benzene and converted to its amide with ammonium hydroxide *via* the acid chloride. The amide recrystallized from benzene–petroleum ether melted at 102–104° (lit.[11] 105°).

Saturation of the aqueous phase with NaCl followed by extraction with ether gave the glutaric acid fragment which recrystallized readily from benzene; m.p. 94–95°. The melting point was not changed when this material was admixed with an authentic sample of glutaric acid.

(b) *trans*-**Tridecen-6-al (X)** (3 g.) was ozonized and oxidized to a mixture of mono- and dicarboxylic acids as described above. When the mixture was triturated with a few ml. of benzene and allowed to stand at room temperature, adipic acid (m.p. 150–152°) separated. This material proved to be identical with an authentic sample.

(c) *trans*-**Tridecen-7-al (XI).**—The oxidative degradation of this aldehyde (3 g.) was carried out in the manner described above. The crystals (m.p. 101–102°) which separated from benzene were compared with an authentic sample of pimelic acid and shown to be identical.

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