The Oxo Reaction of Unconjugated α, ω-Diolefin

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The reaction of olefin with carbon monoxide and hydrogen to form aldehyde is well known as the oxo reaction or hydroformylation.[1] In this reaction, it is not only desirable but also interesting to study whether it is possible to prepare dialdehyde from diolefin.

It has, however, been reported that a conjugated diolefin, such as butadiene and 1, 3-pentadiene, yields not dialdehyde, but saturated monoaldehyde under oxo conditions.[2] Also, it has been reported that an unconjugated cyclic diolefin, such as 4-vinylcyclohexene and dicyclopentadiene, gives a mixture of mono- and dialdehydes in a low selectivity.[3] On the other hand, the reaction of an unconjugated α, ω-diolefin has not been thoroughly studied. From this standpoint, we have been interested in the reaction with 1, 4-pentadiene and 1, 5-hexadiene in order to synthesize dialdehydes and have found that the dialdehydes can be obtained as a main product from the unconjugated α, ω-diolefins under suitable conditions.

It was found essential to carry out the reaction at a lower temperature (below 100°C), in a dilute alcoholic solution and in the presence of a rhodium catalyst instead of the cobalt catalyst usually used in the oxo reaction. The use of a cobalt catalyst or of other solvents resulted in a lower yield of dialdehyde.

After the reaction had been carried out under the conditions cited above, the reaction mixture was catalytically hydrogenated, because it is easier to isolate the reaction products as saturated aldehydes when unsaturated ones are also present. Then the reaction products were identified by converting them into 2, 4-dinitrophenylhydrazones and other derivatives of the corresponding saturated aldehydes.

From 1, 4-pentadiene pimelaldehyde was obtained as a main product in addition to monoaldehydes and other aldehydes in the presence of a rhodium oxide catalyst, but cyclohexanecarboxaldehyde was obtained in the presence of a rhodium chloride catalyst, which generates hydrogen chloride in the course of the reaction. Cyclohexanecarboxaldehyde is formed by an intramolecular aldol condensation of the dialdehyde. As supporting evidence, cyclohexene-1-carboxaldehyde was isolated as the hydrazone in another run. Pimelaldehyde was converted by reduction with lithium aluminum hydride to 1, 7-heptanediol, which was identified as diacetate by comparing the NMR- and infrared-spectra and retention time of its gas chromatograph with those of an authentic sample.

2-Methylheptanedial was obtained from 1, 5-hexadiene as a main product. The dialdehyde was converted by permanganate oxidation to the corresponding diacid and was identified as its dimethylester.

Interestingly, it has already been reported that monoölefin forms mainly branched-chain aldehyde,[4] but in our experiments pimelaldehyde and 2-methylheptanedial were obtained from 1, 4-pentadiene and 1, 5-hexadiene respectively. This suggests that these diolefins form the complexes with the rhodium carbonyl suitable for the 1, 5-insertion of carbon monoxide and that the migration of the double bond[1] into the conjugated position does not take place.

Even under these conditions, butadiene and 1, 3-pentadiene did not give dialdehyde, but only monoaldehyde.

Experimental[5]

The Reaction of 1, 4-Pentadiene.—1, 4-Pentadiene (1.36 g.) prepared from 1, 5-pentanediol diacetate by pyrolysis,[6] rhodium oxide (0.5 g.) and ethanol (50 ml.) were charged in a 200 ml. stainless steel pressure reactor. Air was removed, and a carbon monoxide-hydrogen mixture (1 : 1) was introduced up to the pressure of 150 kg./cm^2. The reaction was carried out at 60$\sim$100°C for 15 min., during which time a pressure drop of 15 kg./cm^2 was observed. The gas mixture was released, the carbonyl catalyst was decomposed, and the reaction mixture was hydrogenated at room temperature

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[1] I. Wender and H. W. Sternberg, "Catalysis," Vol. V, Ed. by P. H. Emmett, Reinhold, New York (1957), p. 73.

[2] H. Adkins and J. L. R. Williams, *J. Org. Chem.*, **17**, 980 (1952).

[3] U. S. Pat. 2810748 (1957); Brit. Pat. 808124 (1959); Brit. Pat. 750144 (1956).

[4] Brit. Pat. 801734 (1958); German Pat. 953605 (1956).

[5] All melting points and boiling points are uncorrected. The microanalyses were performed by analytical division in the Laboratories. IR- and NMR-spectra were obtained using a Shimadzu Model IR-27 and a Varian Model HR-60, respectively. Materials were obtained from commercial sources.

[6] "Organic Syntheses," Vol. **38**, 78 (1958).

under atmospheric pressure over a platinum catalyst. Then, the reaction mixture was treated with 2, 4-dinitrophenylhydrazine in an acidic ethanol solution, giving 5 g. of a hydrazone mixture.

The portion of the hydrazone more soluble in benzene was separated and purified by neutral alumina column chromatography and was recrystallized from ethanol, giving 0.7 g. of yellow crystals, a mixture of the hydrazones of monoaldehydes (m. p. 95∼98°C).

Found: C, 51.54; H, 5.71. Calcd. for $C_{12}H_{16}N_4O_4$; C, 51.42; H, 5.75%.

The portion less soluble in benzene was the hydrazone of cyclohexanecarboxaldehyde (0.5 g., m. p. 169∼170°C), and no depression of melting point was observed with an authentic sample prepared by the hydroformylation of cyclohexene.

Found: C, 53.28; H, 5.49. Calcd. for $C_{13}H_{16}N_4O_4$: C, 53.42; H, 5.52%.

When rhodium chloride was used as a catalyst instead of rhodium oxide, cyclohexanecarboxaldehyde was a main product and the hydrazone of 1-cyclohexene-1-carboxaldehyde was isolated on treating the reaction mixture with 2, 4-dinitrophenylhydrazine without hydrogenation (red crystals of m. p. 214°C decomp., (lit.[7] 215°C decomp.)).

Found: C, 53.56; H, 4.87. Calcd. for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86%.

The portion insoluble in benzene was further fractionated by recrystallization from dimethylformamide. The portion less soluble was considered to be the hydrazone of branched-chain dialdehyde (0.8 g., m. p. 214∼216°C).

Found: C, 47.20; H, 4.16. Calcd. for $C_{19}H_{20}N_8O_8$: C, 46.72; H, 4.13%.

The portion more soluble was a main product identified with the hydrazone of pimelaldehyde (1.6 g., m. p. 177∼179°C (lit.[8] 180∼181°C), and no depression of melting point was observed with an authentic sample prepared by the Rosenmund reduction of pimeloyl chloride.

Found: C, 46.81; H, 4.10. Calcd. for $C_{19}H_{20}N_8O_8$: C, 46.72; H, 4.13%.

In another run, the reaction mixture was poured into water and extracted with ether. The ether layer was dried, the extact was reduced with lithium aluminum hydride, and the dialcohol boiling between 140 and 150°C at 8 mmHg was collected (0.5 g. from 1.36 g. of diolefine). The dialcohol was converted into the diacetate and purified by "Megachrom." The identity of the product with an authentic sample of 1, 7-heptanediol diacetate was confirmed by comparing the retention time of their gas chromatographs and the NMR- and infrared-spectra. NMR-spectra: CH_2O, $6.10\,\tau$ and $6.58\,\tau$; CH_3CO, $8.07\,\tau$; CH_2, $8.62\,\tau$.

An authentic sample of 2, 4-dinitrophenylhydrazone of pimelaldehyde was synthesized in the following way. Pimelic acid (8 g.) was converted into acyl chloride by treatment with oxalyl chloride in benzene. The acyl chloride was reduced in xylene (35 ml.) in the presence of 5% palladium on barium sulfate (1 g.) and "Quinoline-S" (0.1 ml.) at 150∼160°C by bulbbling a hydrogen stream until no more hydrogen chloride was evolved. The catalyst was then removed, and the reaction mixture was treated with 2, 4-dinitrophenylhydrazine. The hydrazones obtained (1.2 g.) were separated into the red hydrazone of cyclohexene-1-carboxaldehyde (0.6 g., m. p. 218°C (decomp.)) and the yellow hydrazone of pimelaldehyde (0.5 g., m. p. 177∼178°C).

The Reaction of 1, 5-Hexadiene.—The reaction of 1, 5-hexadiene (1.65 g.) prepared from allyl magnesium bromide[9] was carried out for 20 min. at 60∼100°C in the same way as with 1, 4-pentadiene. The reaction mixture was hydrogenated and treated with 2, 4-dinitrophenylhydrazine. 3.6 g. of hydrazones were obtained. The hydrazones were fractionated and recrystallized to give the following products; the hydrazones of monoaldehydes (0.8 g.; m. p. 96∼100°C. Found: C, 53.20; H, 5.98. Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.05; H, 6.16%), the hydrazone of suberaldehyde (0.6 g., melting point and mixed melting point with an authentic sample prepared by ozonolysis of cyclooctene 177°C (lit. 175°C,[10] 167∼169°C[8])). Found: C, 47.30; H, 4.46. Calcd. for $C_{20}H_{22}N_8O_8$: C, 47.77; H, 4.41%), and the hydrazone of 2-methylheptanedial (1.3 g. obtained at a main product; m. p. 185°C (unreported). Found: C, 47.81; H, 4.38. Calcd. for $C_{20}H_{22}N_8O_8$: C, 47.77; H, 4.41%).

In another run, the reaction mixture was poured into water and extracted with ether, and then the ether was replaced by acetone. The acetone solution was oxidized with an aqueous permanganate solution to give the dicarboxylic acid. After esterification, 0.6 g. of pure dimethyl 2-methylheptanediate (b. p. 90∼92°C/5 mmHg) was obtained from 1.67 g. of diene and was identified by comparing the infrared- and NMR-spectra and the retention time in its gas chromatography with those of an authentic sample, which had in turn been prepared from dimethyl pimelate and methyl iodide in the presence of sodium alcoholate.[11] The NMR-spectra ($CHCl_3$); OCH_2, $6.34\,\tau$; CH_2CO and CHCO, $7.75\,\tau$; CH_3, $8.50\,\tau$; CH_3, $8.85\,\tau$.

Summary

Pimelaldehyde and 2-methylheptanedial have been obtained from 1, 4-pentadiene and 1, 5-hexadiene respectively by carrying out the oxo reaction in alcohol at a lower temperature (below 100°C) using a rhodium catalyst.

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[7] D. T. C. Gillespie, P. R. Jeffevies, A. K. Macbeth and M. J. Thompson, *J. Chem. Soc.*, **1955**, 665.

[8] W. Treib and R. Helbig, *Chem. Ber.*, **92**, 1559 (1959).

[9] "Organic Syntheses," Coll. Vol., **3**, 121 (1955).

[10] H. J. Bestmann and H. Schulz, *Chem. Ber.*, **92**, 530 (1959).

[11] W. Dieckman, ibid., **33**, 2683 (1900).