

# CLEMMENSEN REDUCTION AND NITRIC ACID OXIDATION OF SOME ALDIMETHONES

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## SUMMARY

Clemmensen reduction of aldimethones (formal-, acetal-, *n*-butyral-, and benzal-dimethones) have yielded the correspondingly 9-substituted tetramethyloctahydroxanthenes. In the case of crotonaldimethone, saturation of the exocyclic double bond also occurred during this reduction and the product obtained was the same as the one from *n*-butyral-dimethone.

Nitric acid oxidation of formal- and acetal-dimethones yielded  $\beta\beta$ -dimethylglutaric acid while oxidation of benzaldimethone yielded a mixture of  $\beta\beta$ -dimethylglutaric acid and nitrobenzoic acids.

Aldimethones (Vorländer, *Z. anal. Chem.*, 1929, 77, 241; *Z. angew. Chem.*, 1929, 42, 46; Klein and Linser, *Mikrochem. Pregl Festschr.*, 1929, pp. 204-34; cf. *Characterisation of Organic Compounds* by F. Wild, 1947 edition, p. 135) are the normal characteristic products obtained by the condensation of aldehydes with methone, i.e., 5:5-dimethyldihydroresorcinol (Vorländer, *Annalen*, 1897, 294, 300; cf. *Organic Synthesis*, 1935, 15, 15), when one molecule of the aldehyde reacts with two molecules of methone. Exceptions to this reaction have been observed: *o*-amino-, and *o*-acetamino-benzaldehydes reacted with methone only in monomolecular proportions yielding acridine and benzhydrol derivatives respectively (Iyer and Chakravarti, *J. Indian Inst. Sci.*, 1931, 14 A, 157).

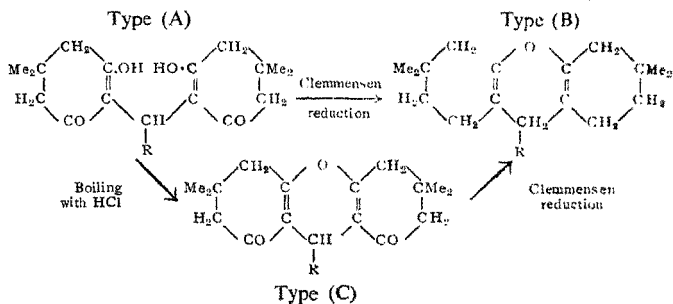
## CLEMMENSEN REDUCTION OF ALDIMETHONES

Qudratikhuda (*Nature*, 1933, 132, 210) has claimed that by Clemmensen reduction of methone he obtained a new ketone isomeric with the already known 1:1-dimethyl-*cyclo*-hexanone-3. From their study on the hydrogenation of 1:3-diketones, Sprague and Adkins (*J. Amer. Chem. Soc.*, 1934, 56, 2669-75) have observed that hydrogenation of methone at 125° C. in presence of Raney's nickel catalyst gave 3.8 per cent. yield of 3:3-dimethyl-*cyclo*-hexanol-1 and 80 per cent. yield of 5:5-dimethyl *cyclo*-hexane-1:3-diol, the latter in two stereo-isomeric forms. The results of Clemmensen reduction of methone by Dey and Linstead (*J.C.S.*, 1935, 1063) were different from those obtained by Qudratikhuda (*loc. cit.*). These authors obtained 1:1:3-trimethyl-*cyclo*-pentane and 2:4:4-trimethyl-*cyclo*-pentanone, resulting from a contraction of the *cyclo*-hexane ring to *cyclo*-

pentane ring during the process of reduction. Wibout and Gitsels (*Rec. trav. chim.*, 1941, **60**, 577) have observed that when methone is reduced catalytically in presence of platinum prepared according to Adams, there is formed about 58 per cent. of the theoretical amount of 3:3-dimethyl-cyclo-hexanol and 10 per cent. of the theoretical amount of 1:1-dimethyl-cyclo-hexane. Henshall (*J. Soc. Chem. Ind.*, 1943, **62**, 127) studied the catalytic reduction of methone in presence of Raney's nickel at 180° C. and at a pressure of 100 atmospheres for six hours when he obtained 75 per cent. of 3:3-dimethyl-cyclo-hexanol-1 and some 5:5-dimethyl-cyclo-hexane-1:3-diol. Sprague and Adkins (*loc. cit.*) have outlined the possibility of formation of twenty different products by the action of hydrogen upon a single unsymmetrical 1:3-diketone.

The present series of experiments were undertaken to see if ring contraction occurred during Clemmensen reduction of aldimethones where the reactive methylene group of methone is anchored through combination with an aldehyde molecule.

When the aldimethones (I), (II), (III), (IV) and (V) of type (A) formed from formaldehyde, acetaldehyde, *n*-butyraldehyde, crotonaldehyde and benzaldehyde respectively, were submitted to Clemmensen reduction, the corresponding octahydroxanthenes (VI), (VII), (VIII) and (IX) of type (B) were obtained. Apparently, formation of the corresponding anhydride, type (C), preceded the process of reduction. This was proved by the formation of the same xanthene derivative (VI) in a test experiment when the anhydride of formaldimethone (I) [type (C) where R = H], was reduced in the Clemmensen way. In the case of croton-aldimethone (IV) Clemmensen reduction brought about the saturation of the exocyclic double bond also, thus leading to the formation of the same xanthene derivative (VIII) as the one obtained from *n*-butyraldimethone (III).



## Guide to Formulae

Type (A)	Type (B)	R stands for
I	VI	H
II	VII	CH <sub>3</sub> -
III	VIII	CH <sub>3</sub> .CH <sub>2</sub> .CH <sub>2</sub> -
IV	do.	do.
V	IX	C <sub>6</sub> H <sub>5</sub> -

Since Clemmensen reduction involves the use of hydrochloric acid, it was postulated that anhydride formation was due to this acid. This has been confirmed by the formation of its anhydride when formaldimethone (I) was heated with hydrochloric acid during one hour. Klein and Linser (*loc. cit.*) prepared the anhydrides by boiling the aldimethones with 40 per cent. sulphuric acid for two hours.

The present observations would indicate that the fixing of the two methone molecules through the formation of aldimethones and anhydrides prevented the ring contraction of the *cyclo*-hexane ring during Clemmensen reduction.

## NITRIC ACID OXIDATION OF ALDIMETHONES

Oxidation of methone with dilute nitric acid or potassium-dichromate and sulphuric acid (Crossley, *J.C.S.*, 1899, **75**, 777), with alkali hypochlorites (Vorländer and Kohlmann, *Annalen*, 1902, **322**, 246, 258; Walker and Wood, *J.C.S.*, 1906, **89**, 599; and Komppa, *Annalen*, 1909, **368**, 135), and with sodium hypobromite (Komppa, *Ber.*, 1899, **32**, 1423; Vorländer and Kohlmann, *Ber.*, 1899, **32**, 1879; *Annalen*, 1902, **322**, 249) as also heating of methone with fuming hydrochloric acid at high temperature (Haas, *J.C.S.*, 1906, **89**, 200) have led to the formation of  $\beta\beta$ -dimethylglutaric acid. Oxidation with potassium permanganate has yielded 2:2-dimethylsuccinic acid (Vorländer and Gärtner, *Annalen*, 1899, **304**, 15).

In the present investigation, oxidation of formaldimethone (I) and acetal-dimethone (II) with dilute nitric acid (1:2) yielded only  $\beta\beta$ -dimethylglutaric acid characterised by comparison with a genuine sample. Benzal-dimethone (V) however yielded a mixture of  $\beta\beta$ -dimethyl glutaric acid and nitrobenzoic acids indicating that nitration of the aromatic ring also occurred during oxidation.

## EXPERIMENTAL

The aldimethones were prepared by known methods (*cf.* Wild, *loc. cit.*).

*Formation of 3 : 3 : 6 : 6-tetramethyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroxanthene (VI) from formaldimethone (I).*—Formaldimethone (I) (15 g.) was refluxed for 18 hours with amalgamated zinc (50 g.) and concentrated hydrochloric acid (90 c.c.). The solution, at first clear, became opalescent, and then brownish; finally an oily layer separated. This was taken up in ether and the extract washed with dilute alkali and water, and dried with  $\text{CaCl}_2$ . After removal of ether the residue was distilled under reduced pressure and the product isolated: b.p., 128–30°/6 mm.; refractive index at 24° C. = 1.484; insoluble in acid and alkali; possesses a camphoraceous smell; soluble in alcohol and chloroform; sparingly soluble in benzene and toluene. (Found: C = 83.35; H = 10.08;  $\text{C}_{17}\text{H}_{26}\text{O}$  requires C = 83.6; H = 10.33 per cent.)

*Dehydration of aldimethone with concentrated hydrochloric acid.*—Formaldimethone (I) (10 g.) was heated under reflux with concentrated hydrochloric acid (30 c.c.) for one hour and the resulting product was filtered after cooling and dilution of the reaction mixture. The product was washed with alkali and water, and crystallised from alcohol; m.p., 170° C. A mixed melting point of this with the anhydride prepared by using 40 per cent. sulphuric acid as the dehydrating agent showed no depression.

*Formation of (VI) from formaldimethone anhydride (Type C, R = H).*—The anhydride (10 g.) was heated under reflux with amalgamated zinc (30 g.) and concentrated hydrochloric acid (60 c.c.) for 20 hours and the product was isolated and identified as (VI) described in the first experiment.

*Formation of 3 : 3 : 6 : 6 : 9-pentamethyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroxanthene (VII) from acetaldimethone (II).*—Acetaldimethone (10 g.) was reduced with amalgamated zinc (40 g.) in concentrated hydrochloric acid (80 c.c.) and the product isolated as above; b.p., 80–82° C.; soluble in alcohol and chloroform; insoluble in benzene and toluene. (Found: C = 83.9; H = 10.8;  $\text{C}_{18}\text{H}_{28}\text{O}$  requires C = 83.08; H = 10.77 per cent.)

*Formation of 3 : 3 : 6 : 6-tetramethyl-9-propyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroxanthene (VIII) from n-butyraldimethone (III).*—Butyraldimethone (15 g.) was reduced with amalgamated zinc (50 g.) and concentrated hydrochloric acid (100 c.c.) during 20 hours and the product isolated as above; b.p., 184°/6 mm. (Found: C = 82.2; H = 12.12;  $\text{C}_{20}\text{H}_{32}\text{O}$  requires C = 83.3; H = 11.11 per cent.)

*Formation of above (VIII) from crotonaldimethone (IV).—*Crotonaldimethone (15 g.) was reduced with amalgamated zinc (50 g.) and concentrated hydrochloric acid (100 c.c.) during 24 hours and the product isolated and characterised as (VIII).

*Formation of 3:3:6:6-tetramethyl-9-phenyl-1:2:3:4:5:6:7:8-octahydroxanthene (IX) from benzaldimethone (V).—*Benzaldimethone (15 g.) was reduced with amalgamated zinc (50 g.) and hydrochloric acid (100 c.c.) during 30 hours and the product isolated as above; b.p., 220°/60 mm.; 193–94°/6 mm. (Found: C = 85.67; H = 9.5;  $C_{23}H_{30}O$  requires C = 85.71; H = 9.32 per cent.)

*Oxidation of formaldimethone (I); formation of  $\beta\beta$ -dimethylglutaric acid.*—Formaldimethone (5 g.) was heated under reflux with six times its weight of dilute nitric acid (1:2). The mixture gradually changed in colour and after half an hour became cherry red. Then the oxidation became vigorous and after another half an hour it was completed. Nitric acid was then removed by evaporation on a water-bath and the residual solid was crystallised from benzene; m.p., 100–101° C. This was characterised as  $\beta\beta$ -dimethylglutaric acid from a mixed melting point with a genuine sample of the acid and also by converting it into its anhydride.

Acetaldimethone (II) also gave  $\beta\beta$ -dimethylglutaric acid on similar treatment.

*Oxidation of benzaldimethone (V).—*The solid residue obtained from benzaldimethone (5 g.) on oxidation with nitric acid as above, was characterised as a mixture of  $\beta\beta$ -dimethylglutaric acid and nitrobenzoic acids. Separation of these acids was difficult.

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