# REDUCTION OF ESTER GROUPINGS IN PORPHYRINS WITH SODIUM BOROHYDRIDE

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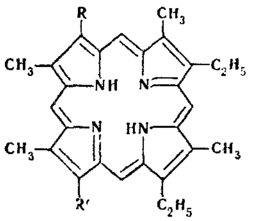
Reduction of the corresponding acyl derivatives by means of sodium borohydride [1, 2] is usually employed to obtain porphyrins with α-hydroxyalkyl substituents.

During the reduction of the acetyl group in 1,3,5,8-tetramethyl-4,6-diethyl-7-(2-carbomethoxyethyl)-2-acetylporphyrin (I) (mp 255-257°C), we found that the solvent used in the reaction has a great effect on the direction of the reduction. Thus maintaining porphyrin I at room temperature in tetrahydrofuran in the presence of excess sodium borohydride for 4 h gives porphyrins II (mp 235-238°) and III (mp 227-228°) in yields of 33.2 and 32.6%, respectively, while III is obtained in 91.5% yield after 12 h. Under the same conditions, porphyrin IV (mp 258-260°) is reduced to porphyrin V (mp 248-250°) in 82.8% yield.



| Compound | R | R' |
|---|---|---|
| I | $COCH_3$ | $CH_2CH_2COOCH_3$ |
| II | $CH(OH)CH_3$ | $CH_2CH_2COOCH_3$ |
| III | $CH(OH)CH_3$ | $CH_2CH_2CH_2OH$ |
| IV | H | $CH_2CH_2COOCH_3$ |
| V | H | $CH_2CH_2CH_2OH$ |
| VI | $CH(OH)CH_3$ | $CH_2CH_2CH_2OSO_3H$ |
| VII | H | $CH_2CH_2CH_2OSO_3H$ |
| VIII | H | $CH_2CH{=}CH_2$ |

The reduction of ester groups that is observed in this case probably occurs through the activating effect of the porphyrin ring, since reduction of a model compound – ethyl hydrocinnamate – does not occur at all under similar conditions.

Selective reduction of the acetyl group in porphyrin I was accomplished by carrying out the reaction in dimethylformamide for 2 h at 40° (the yield was 58% based on converted starting porphyrin) and also after 4 h in pyridine (the yield was 61.6%). In the latter case, the carbomethoxy group underwent partial saponification.

A characteristic feature of the mass spectra of porphyrins III and V is the presence of a molecular-ion peak $M^+$ (m/e 480, 100%) for V and an $[M-H_2O]^+$ ion peak (m/e 506, 100%) for III, which is formed due to splitting out of water from the α-hydroxyethyl group. The complete absence of ion peaks with m/e 462 for V and 488 for III indicates the high stability of the γ-hydroxypropyl residue in the porphyrin molecule. Similar fragmentation was also observed for the corresponding copper complexes of III and V.

For confirmation of the structures of porphyrins III and V, they were dissolved in cold concentrated sulfuric acid, in which the corresponding esters – sulfates VI and VII with mp > 200° (with decomposition) – are slowly formed. These compounds are stable in methanol, pyridine, and other polar solvents. Treatment of sulfates VI and VII for 12 h with 5% sulfuric acid in methanol regenerates free alcohols III and V.

The ion peak with m/e 462, $[M-H_2SO_4]^+$, has the maximum intensity in the mass spectrum of porphyrin VII, while the molecular-ion peak is absent. Thermal dissociation of sulfate VII in the ion source of the spectrometer, which leads to the formation of propenyl derivative VIII, probably occurs in this case, and its molecular-ion peak with m/e 462 appears in the mass spectrum.

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