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Note

Synthesis of 1, 5-Dialdehydonaphthalene by the Sommelet Reaction

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Introduction

The Sommelet reaction has been known as a method of the formation of aldehydes by the reaction of aryl methyl (or alkyl) halides with hexamethylenetetramine. Wood[1] had synthesized some new aromatic dialdehydydes by this method. However, no references concerning with the preparation of polynuclear aromatic dialdehyde by the Sommelet reaction can be found.

Only 4, 4′-dichloromethyl diphenyl[2], 1, 5-dichloromethyl naphthalene[3], and 9, 10-dichloromethyl anthracene[4] and 1, 8-dialdehydonaphthalene[5] have been reported. The need for polynuclear aromatic dialdehydes, being useful monomers for the synthesis of polymers, promoted for the author to undertake a study of introducing two aldehyde groups into a naphthalene nuclei. The present work describes the formation of hexamethylenetetramine-1, 5-dichloromethyl naphthalene salt and hydrolysis of it into 1, 5-dialdehydonaphthalene by the utilization of the Sommelet reaction.

Experimental

Formation of hexamethylenetetramine-1, 5-dichloromethyl naphthalene salt. Dichloromethylation of naphthalene was carried out as follows[3].

Ninety grams of naphthalene was added into 243.2 gr. of an aqueous solution of formaldehyde (36%) and 200gr. of concentrated hydrochloric acid with stirring. Then the dissolved mixture was refluxed for 13 hours while stirring and a gentle current of dried hydrochloric acid gas introduced.

As the reaction was proceeded, the reaction mixture was colored gradually into yellow. After the reaction was completed, the reaction mixture was cooled, filtered and washed with water throughly. Then white solid mass was isolated from the recrystallization in acetone. Yield; 32 gr. (20%). m. p., 135–37°C (lit[3]., 130–40°C).

Hexamethylenetetramine (2.8 gr.) and 1, 5-dichloromethyl naphthalene (2.25gr.) were dissolved separately in 50ml. of dry chloroform. After brining two chloroform solutions together, the mixture was refluxed for 5 hours until the precipitation was completed. After cooling, water soluble yellow hexamium salt was isolated by filtration, and washed with dry chloroform and dried to give 4.7 gr. of hexamium salt.

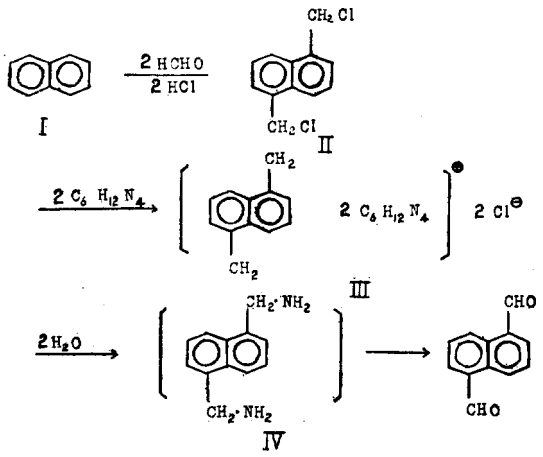
Preparation of 1, 5-dialdehydonaphthalene.

A solution of the hexamium salt (3.5 gr.)

in 120 ml. of water was refluxed for 7 hours. After filtration and washing with cold water, slight yellow crystal was isolated. A recrystallization from ethanol gave 1.0 gr. of the yield (52 %), m.p. 168–70°C (decomp.). Anal. Calcd for $C_{12}H_8O_2$: C, 72.79 %; H, 4.32 %. Found: C, 72.51 %; H, 3.85 %. All the melting points measured were uncorrected.

Results and Discussion

The preparation of 1, 5-dialdehydonaphthalene was carried out by the Sommelet reaction. Starting 1, 5-dichloromethyl naphthalene was obtained by the action of formaldehyde and dry hydrochloric acid. One mole of 1, 5-dichloromethyl naphthalene reacted with two moles of hexamethylenetetramine to afford a quantitative yield of the quaternary hexamium salt in refluxing chloroform. Then 1, 5-dichloromethyl naphthalene-hexamethylenetetramine salt was hydrolysed initially to an arylmethyl amine and then into 1, 5-dialdehydonaphthalene.



Reaction Scheme

An IR absorption of (Ⅲ) at 3300cm^{-1} might be attributable to the quaternary amine group. The hexamium salt (Ⅲ) obtained was not soluble in chloroform but completely soluble in water. Such fact supports strongly the formation of hexamium salt. An attempt to isolate the intermediate amine (Ⅳ) was not succeeded. 1, 5-dialdehydonaphthalene obtained from (Ⅳ) showed an intensive absorption at 1680 cm^{-1} attributed to $\nu c{=}o$.

The high melting point of 1, 5-dialdehydonaphthalene, as contrasted with that of *cis*-form, 1, 5-dialdehydonaphthalene (m.p.; 130°C)[5], is quite reasonable. The elementary analysis of (Ⅴ) gave also satisfactory results.

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