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AN ANAMOLOUS REACTION PRODUCT IN VILSMEIER-HAACK REACTION

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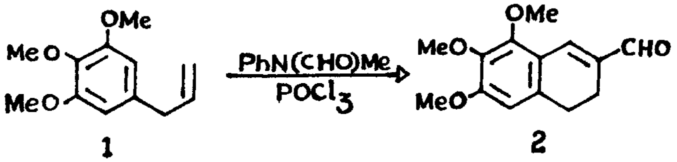
Summary : A Vilsmeier-Haack formylation is reported in which reduction has occurred with the methyl group of the reagent functioning as hydrogen donor.

We report below an intriguing reaction where, in a Vilsmeier-Haack reaction, not only formylation occurred but also reduction. Thus, when the trimethoxy allyl benzene 1 was treated with the Vilsmeier-Haack reagent [from $PhN(CHO)CH_3$ and $POCl_3$], a compound was obtained whose spectral data indicated it to be 2 or 3. The nOe experiments [$f_{Ar-H}(Ar-CH_2-) = 17\ \%$, $f_{Ar-H}(OMe) = 16\ \%$, $f_{Ar-H}(=CH-) = f_{-CH=}(Ar-H) = 0\ \%$] indicated that the aromatic proton was flanked by a methoxyl group on one side and a $-CH_2-$ group, and not a = CH- group, on the other. This indicated uniquely to structure 2 for the compound.*



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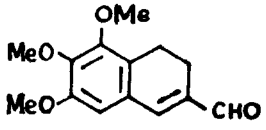

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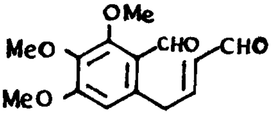
An examination of the Vilsmeier-Haack reaction product 2 showed that formylation had occurred at two positions in compound 1. The anticipated structure corresponding to double formylation and resembling the carbon skeleton in compound 2 was 4 or 5 or the cyclised naphthalene derivative 6.



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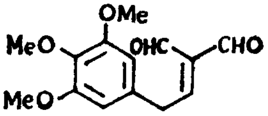

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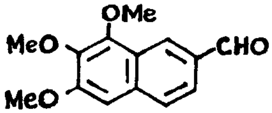

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The formation of the dihydro compound 2, clearly indicated that a reduction had occurred during the reaction.

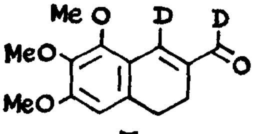
A priori, the hydrogen in the reduction reaction could have been from (i) another molecule of the starting compound or a product derived from it (a disproportionation reaction) (ii) the formyl group of PhN(CHO)CH_3, (iii) the methyl group of PhN(CHO)CH_3 or (iv) the water used during the work-up.

Compound 2 was obtained in not less than 58 % yield, ruling out any disproportionation reaction.

When the Vilsmeier-Haack reaction was carried out with PhN(CDO)CH_3, deuterium incorporation occurred only at the expected position of formylation to give compound 7.

When D_2O was used to decompose the Vilsmeier-Haack reaction mixture, no deuterium incorporation occurred.

Finally, when the Vilsmeier-Haack reaction was carried out with PhN(CHO)CD_3 one atom of deuterium was incorporated to give compound 8 [NMR data and dehydrogenation to 9a (R=H) and 9b (R=D)] , indicating that the hydrogen involved in the reduction was from the methyl group of PhN(CHO)CH_3.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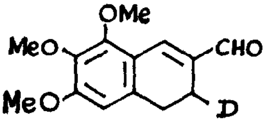
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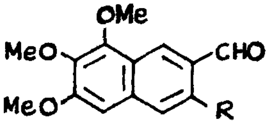
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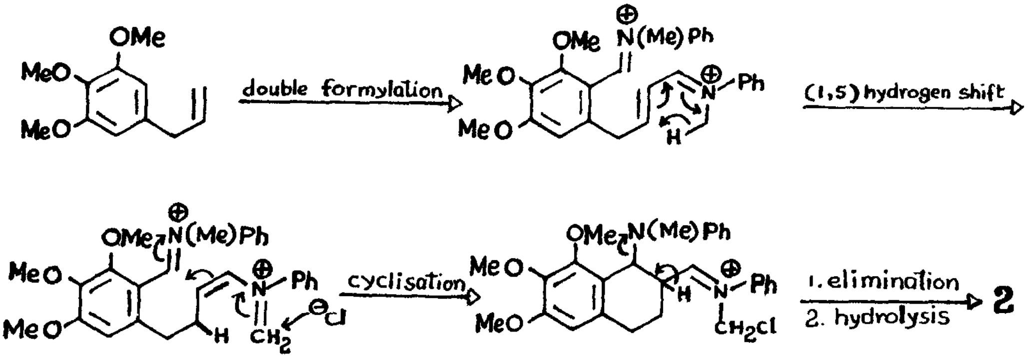
We propose the following attractive mechanism for this novel reaction.



Experiments are in progress to trap the intermediates in the reaction.

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