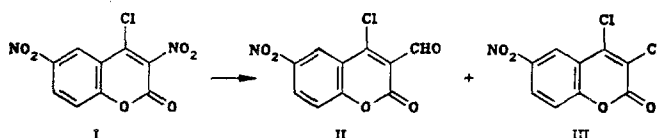


SUBSTITUTION OF A NITRO GROUP BY FORMYL OR A CHLORINE ATOM IN
3,6-DINITRO-4-CHLOROCOUMARIN UNDER VILSMEIER-HAACK CONDITIONS

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Heating 3,6-dinitro-4-chlorocoumarin (I) with excess phosphorus oxychloride in absolute DMF unexpectedly led to two novel products, viz. 3-formyl-4-chloro-6-nitrocoumarin (II, mp 172-174°C) and 3,4-dichloro-6-nitrocoumarin (III, mp 168-170°C) which could be separated chromatographically on silica gel. Similar results were obtained with 3,6-dinitro-4-hydroxycoumarin but 3-nitro-4-chlorocoumarin was practically unchanged under these conditions.



The structures of II and III were confirmed by elemental analysis, IR and PMR spectra, and by an independent synthesis via nitration of 3-formyl-4-chlorocoumarin and 3,4-dichlorocoumarin respectively.

To our knowledge the formation of III is the first example of ipso-substitution of a nitro group by formyl under Vilsmeier-Haack conditions.