

# Nitroschlorination of Natural Monocyclic and Bicyclic Sesquiterpenes

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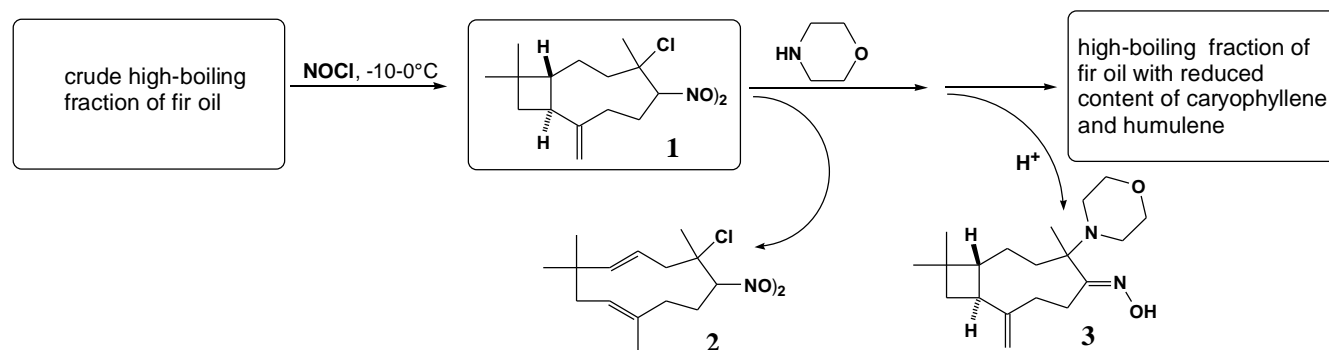
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Essential oils, turpentine and resins of conifers are rich source of many useful terpenic compounds. As a rule, crude oils or extracts are very complex mixtures of terpenoids, that can be separated to several groups such as monoterpenoids, sesquiterpenoids, diterpenoids, resin acids, etc. Mixtures of sesquiterpenoids usually consist of many components whose separation can be carried out only by precise rectification in vacuum. Is it possible to separate these mixtures using simple chemical procedures? We have found that in certain cases the

crude mixtures can be used for preparing of pure derivatives of individual components without preliminary separation.

The oil of *Abies sibirica* Ledeb is one of the most intensively used oils of conifers. Distillation of the oil results in high-boiling residue which is a complex mixture of sesquiterpenoids (Figure on the left, upper drawing). Treatment of the mixture in a solution of methylene chloride with NOCl results in formation of nitroschlorides of caryophyllene (**1**) and humulene (**2**). Crystalline compound **2** is totally insoluble and can be easily separated by filtration. Subsequent treatment of the mixture with morpholine leads to N-morpholinoamino oxime of caryophyllene (**3**) that is extracted with a diluted acid. The remainder is the mixture of high-boiling compounds, containing the reduced amounts of caryophyllene and humulene.

Thus the procedure described is allowed one to prepare nitrogen-containing derivatives of caryophyllene and humulene from crude natural oil without preliminary separation:



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