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FACILE FRAGMENTATION OF PINENES USING DIMETHYL SULFOXIDE ACTIVATED BY PHENYL DICHLOROPHOSPHATE OR PHOSPHORUS OXYCHLORIDE. EFFICIENT CONVERSION OF α-PINENE TO CARVONE

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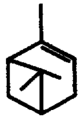
Summary: Treatment of pinenes with dimethyl sulfoxide in the presence of phenyl dichlorophosphate or phosphorus oxychloride resulted in facile fragmentation giving rise to limonene derivatives. The fragmentation reaction serves as a key step in the efficient conversion of α-pinene (**1**) to carvone (**7**).

Recently we reported the formation of β-chloroalkyl sulfides from alkenes by treatment with dimethyl sulfoxide in the presence of phosphorus oxychloride or its phenoxy derivative, phenyl dichlorophosphate.[1] Interestingly, when α-pinene (**1**) (10 mmol) was subjected to treatment with dimethyl sulfoxide (40 mmol) and phenyl dichlorophosphate (20 mmol) or with dimethyl sulfoxide (20 mmol) and phosphorus oxychloride (10 mmol)[2] in methylene chloride (10 mL) for 20 min over a temperature range of -20°C to 20°C, the expected chloroalkyl sulfide was not detected. Instead, a rearrangement product which was characterized as chloride **2**[3] was formed in virtually quantitative yield. Similarly, treatment of β-pinene (**3**) with dimethyl sulfoxide in the presence of phenyl dichlorophosphate or phosphorus oxychloride led to the quantitative formation of the fragmentation product **4**.



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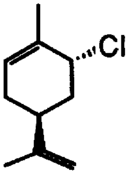

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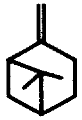

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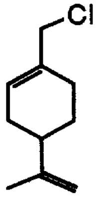

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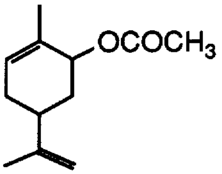
The facile rearrangement of pinenes induced by dimethyl sulfoxide and the phosphorus-containing reagents provides an efficient access to limonene derivatives which are suitably activated for further manipulation. These compounds are potential synthetic precussors for natural products containing an intact or modified limonane framework. As an example, treatment of chloride **2** with silver acetate in refluxing glacial acetic acid for 1 h afforded a mixture of two isomeric acetates **5** in 86% yield. Hydrolysis of acetates **5** with aqueous potassium carbonate in refluxing methanol resulted in the formation of alcohols **6** in quantitative yield.[6] Subsequent oxidation of alcohols **6** with phenyl dichlorophosphate, dimethyl sulfoxide and triethylamine[7] gave an 81% yield of carvone (**7**), a naturally occurring monoterpene which is an important ingredient in flavouring liqueurs, perfumes and soaps.[8] Thus, with the highly efficient rearrangement to chloride **2**, the naturally abundant α-pinene (**1**) was readily converted to carvone (**7**) in four simple synthetic operations in an overall yield of 70%. This new synthetic approach to carvone (**7**) compares favourably with the existing ones[5,9] in terms of operational simplicity and efficiency.



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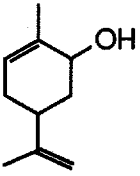

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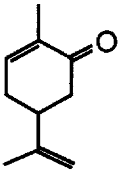

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References and Notes

1. Liu, H.J.; Nyangulu, J.M. *Tetrahedron Lett.*, **1988**, *29*, 5467.
2. Under similar conditions, the combination of oxalyl chloride and dimethyl sulfoxide was found to be ineffective.
3. This compound has been obtained previously from α-pinene in low yield by treatment with chlorine[4] or *tert*-butyl hypochlorite.[5]
4. (a) Kergomard, A. *Ann. Chim.*, **1953**, *8*, 153. (b) Tishchenko, D.; Matveev, B. *Zh. Obsch. Khim.*, **1950**, *20*, 896.
5. Ritter, J.J.; Ginsburg, D. *J. Am. Chem. Soc.*, **1950**, *72*, 2381.
6. Alcohols **6** could also be prepared directly from chloride **2** by treatment with silver oxide, potassium carbonate or sodium hydroxide. However, under a variety of conditions, the best yield obtained was only 30%.
7. Liu, H.J.; Nyangulu, J.M. *Tetrahedron Lett.*, **1988**, *29*, 3167.
8. Windholz, M.; Budavari, S.; Blumetti, R.F.; Otterbein, E.S. "The Merck Index," 10th Ed., Merck and Co. Inc., Rahway, N.J., **1983**, Entry 1856.
9. (a) Suga, T. *Bull. Chem. Soc. Japan*, **1958**, *31*, 569. (b) Fleming, I.; Patterson, I. *Synthesis*, **1979**, 736. (c) Royals, E.E.; Horne, S.E., Jr. *J. Am. Chem. Soc.*, **1951**, *73*, 5856. (d) Booth, A.B.; Klein, E.A. *U.S. Pat.* 2796428, **1957**.

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