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# ISOMERIZATION OF LONGIFOLENE TO ISOLONGIFOLENE CATALYZED BY MONTMORILLONITE CLAY

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# ISOMERIZATION OF LONGIFOLENE TO ISOLONGIFOLENE CATALYZED BY MONTMORILLONITE CLAY

Submitted by
(05/14/97)

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During the last decade, a large number of reactions catalyzed by clays or modified clays have been reported.[1] Laszlo's group[2] has performed pioneering work in exploring the utility of clays in organic transformations. Some of the interesting reactions catalyzed by clay include nitration,[3] Michael addition,[4] Friedel-Crafts reaction[5] and oxidations[6] and these reactions are becoming quite popular in academic as well as industrial research owing to the simpler reaction conditions and eco-friendly nature. The acidic clays also have the advantage that reaction may be carried out without recourse to any special reaction vessel (a matter of great concern for an industrial scale) unlike the case with protic or Lewis acids.

Isolongifolene (**2**) is an important raw material in the synthesis of many perfumery products having interesting woody fragrances and is a prime constituent of many perfume formulations.[7,8] Existing procedures involve either reacting longifolene (**1**) with protic acids like dilute sulfuric acid[9] or with Lewis acids such as $BF_3 \cdot Et_2O$.[7] All these methods have serious drawbacks during scale-up. Variable proportions of the rearranged products, tetralin **4** and octalin **5**, are unavoidable side-products.[10] The protic acids produce more resinous material while Lewis acids require dry reaction conditions in addition to the formation of resinous material. Although there is a report on the use of Japanese acidic clay for the isomerization of longifolene to isolongifolene at 200°, no information was

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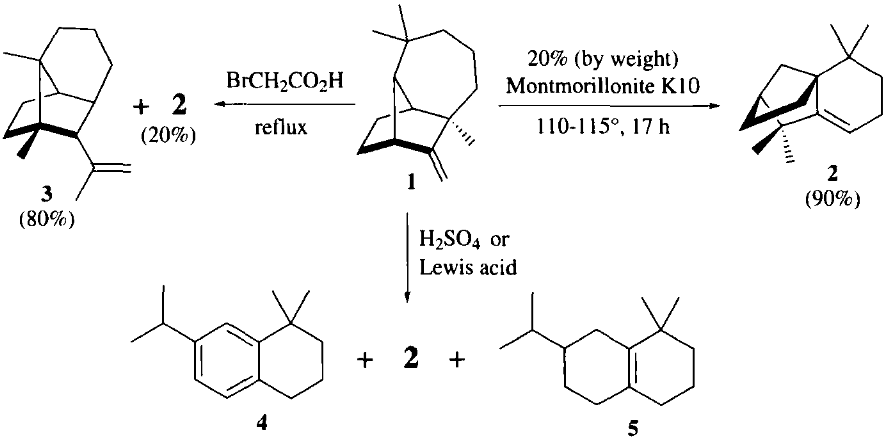

provided about the yield and quality of the product.[11] Longifolene (**1**) can also be isomerized to *allo*isolongifolene (**3**) with bromoacetic acid[12] at reflux temperature. We now report a clean isomerization of longifolene (**1**) to isolongifolene (**2**) catalyzed by montmorillonite K10 clay which has been carried out on a multikilogram scale. Moreover, the reaction conditions are milder, produce no side-products, *viz.* **3**, **4**, or **5** and the work up is very simple. Measurement of optical rotation of the product revealed that extensive racemization occurred during isomerization as expected, also in line with the earlier report.

In a typical experiment longifolene (**1**) was treated with 20% by weight of montmorillonite K10 clay and heated at 110-115° (in contrast to the procedure reported[11] with Japanese acidic clay where it was heated at 200°) for 17 h without the need for an inert atmosphere. Filtration and vacuum distillation of the crude product afforded isolongifolene (**2**) as the only product ascertained to be very pure by GC. Isolongifolene thus obtained exhibits a fine woody odor and can be satisfactorily used in perfumery (in fact, the odor quality of this product exceeds the one produced using $BF_3{\bullet}OEt_2$ procedure[7]). The course of the reaction was followed by $^{13}$C NMR spectroscopy. After 16 h of heating at 110-115°, the $^{13}$C signals corresponding to longifolene double bond disappeared.

Thus the isomerisation of longifolene (**1**) to isolongifolene (**2**) catalyzed by montmorillonite K10 clay is clean, easy to perform and hence offers many advantages over the existing procedures.

## EXPERIMENTAL SECTION

$^{13}$C NMR spectra were recorded in $CDCl_3$. Commercial grade longifolene was distilled prior to use. Montmorillonite K10 clay was purchased from Fluka and was used as such.

**Isomerization of Longifolene.**- Longifolene **1** (1010 g, 5 mole), montmorillonite K10 clay (200 g) were mixed and heated with stirring at 110-115° for 17 h. The reaction mass was cooled and diluted with toluene (800 mL) and filtered. The catalyst was washed with toluene (2 x 200 mL) and this filtrate was concentrated to dryness. Distillation of the residue under vacuum afforded *iso*longifolene (**2**) as the only product (949 g, 90%), bp. 118-120°/8 torr, *lit.*[11] 113-114°/7 torr. GC: $R_t$ 0.88 min.

[Column: FS-Lipodex A (25 m x 0.25 mm ID), Temperature: 140° (isothermal), Detector: FID (temperature: 260°), Carrier gas: $N_2$ (pressure: 1 Kg/cm$^2$)]. $^{13}$C NMR (22.5 MHz, $CDCl_3$): δ 154.87, 110.52, 55.77, 46.53, 41.72, 36.52, 33.68, 30.92, 30.14, 28.71, 26.37, 25.46, 24.68, 24.03, 22.73.

**Data for 1**. GC: $R_t$ 0.82 min. [Column: FS-Lipodex A (25 m x 0.25 mm ID), Temperature: 140° (isothermal), Detector: FID (temperature: 260°), Carrier gas: $N_2$ (pressure: 1 Kg/cm$^2$)]. $^{13}$C NMR (22.5 MHz, $CDCl_3$): (167.36, 99.34, 62.14, 47.96, 45.10, 43.93, 43.41, 36.52, 33.53, 30.53, 30.14, 29.75, 25.59, 21.17.

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# IMPROVED SYNTHESIS OF *bis*(2,2,2-TRIFLUOROETHYL) PHOSPHOROCHLORIDATE

*Submitted by*
(11/09/98)

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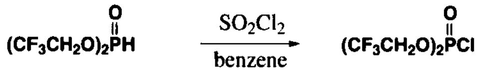
Phosphorochloridate electrophiles have found extensive applications in organic synthesis in the preparation of β-ketophosphonates,[1] α-phosphono lactones and esters,[2] ketene acetal phosphates for use in the Stille coupling,[3] and alkynes[4] amongst many other applications.[5] *bis*(2,2,2-Trifluoroethyl) phosphorochloridate (**1**) has been underutilized as a reagent in organic synthesis, due to the impracticality of the literature method of synthesis.[6] The previous synthesis involved treatment of $P(O)Cl_3$ with trifluoroethanol to yield a mixture of products which included (2,2,2-trifluoroethyl) phosphorodichloridate [$CF_3CH_2OP(O)Cl_2$ (**2**)] which was purified by vacuum distillation. The dichloridate **2** was treated further with trifluoroethanol and compound **1** was isolated after a second vacuum distillation. The problems with this route include low yields and a tedious and difficult separation *via* repeated high vacuum fractional distillations. This paper describes an efficient, one-step synthesis of **1** from commercially available reagents, which may be purified easily by distillation under aspirator or high vacuum to provide pure material in quantitative yield.



$$(CF_3CH_2O)_2\overset{\overset{O}{\|}}{P}H \xrightarrow[\text{benzene}]{SO_2Cl_2} (CF_3CH_2O)_2\overset{\overset{O}{\|}}{P}Cl$$

Our improved synthesis relies on the method first reported by Sosnovsky and Zaret.[7] Addition of a solution of *bis*(2,2,2-trifluoroethyl) phosphite in benzene to a solution of sulfuryl chloride in benzene results in quantitative formation of *bis*(2,2,2-trifluoroethyl) phosphorochloridate (**1**), as determined by both $^{31}P$ NMR spectroscopy and GC analysis. In our lab, typically the product is isolated by distillation under aspirator-induced vacuum to afford pure material.

## EXPERIMENTAL SECTION

$^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on a 400 MHz Varian Gemini 2000 Spectrometer. *bis*(2,2,2-Trifluoroethyl) phosphite and sulfuryl chloride were purchased from Aldrich Chemical Co.

***bis*(2,2,2-Trifluoroethyl) Phosphorochloridate (1)**.- To a solution of *bis*(2,2,2-trifluoroethyl) phos-