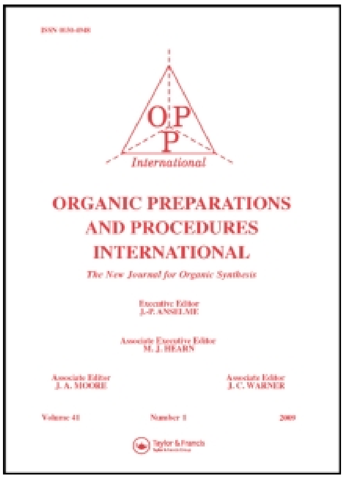

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SYNTHESIS OF DIALLYL SELENIDE

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SYNTHESIS OF DIALLYL SELENIDE

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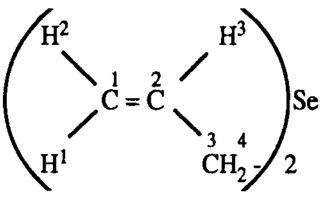
Allylic selenides are useful synthons in organic synthesis.[1] Diallyl selenide (1)[2,3] which is expected to possess high synthetic utility, has been prepared in 58% yield as a mixture with allyl propyl selenide by the interaction of allyl chloride with the system Se-KOH-$N_2H_4 \cdot H_2O$.[3] The shortcoming of this method is that 1 can only be isolated by preparative GLC. We now report a convenient route to diallyl selenide from selenium metal and allyl bromide in 72% yield. This method is based on the generation of a selenide anion from selenium metal in the system KOH-$SnCl_2$-H_2O under phase-transfer conditions.

$$Se + CH_2{=}CHCH_2Br \xrightarrow[PhCH_2\overset{+}{N}Et_3\ Cl^-]{KOH, SnCl_2, H_2O} (CH_2{=}CHCH_2)_2Se$$

1



EXPERIMENTAL SECTION

Diallyl Selenide.- A mixture of powdered selenium (20 g, 0.25 mol), KOH (100 g, 1.79 mol), $SnCl_2 \cdot 2H_2O$ (57 g, 0.25 mol), benzyl triethylammonium chloride (2 g, 0.009 mol) and water (300 ml) was vigorously stirred at 85-90° for 1.5 hr. The mixture was then allowed to cool to 60-65° and allyl bromide (61 g, 0.54 mol) was added dropwise within 0.5 hr. This mixture was stirred for 1.5 hr (60-65°) and extracted with pentane (2 x 60 ml). The organic layer was dried (K_2CO_3) and pentane was evaporated. Distillation of the residue under reduced pressure afforded 29.5 g (72% yield) of pure 1, bp. 75-77°/50 mm, n_D^{25} 1.528. IR (film): 1625 cm^{-1} (C=C). ^1H NMR ($CDCl_3$): δ 5.82 [2 H, m, H(3)], 5.01 [2 H, dd, H(1), J = 0.2, 16 Hz], 4.99 [2 H, dd, H(2), J = 0.2, 10 Hz], 3.13 [4 H, d, H(4), J = 8 Hz]. ^{13}C NMR ($CDCl_3$): 135.0 [C(2)], 116.1 [C(1)], 25.1 ppm [C(3)]. MS: m/z (rel. int., %) 162 (44), 121 (100), 93 (45), 81 (50), 41 (74), 39 (68).

Anal. Calcd for $C_6H_{10}Se$: C, 44.73; H, 6.26; Se, 49.01. Found: C, 44.53; H, 6.15; Se, 48.93

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O-METHYLATION OF POLYMER-SUPPORTED PHENOXIDES WITH DIMETHYL SULFATE

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The alkylation of phenols[1] using ion-exchange polymers benefits from the increased nucleophilicity of the polymer-supported anions. Although the O-methylation of polymer-supported phenoxides using methyl iodide is successful in some cases, it does not always result in high yields of products. Moreover, apart from inherent inconveniences in the use of methyl iodide (low volatility and greater cost of the reagent), the reaction may take a long time for completion.[2] We have found that dimethyl sulfate is much more effective than methyl iodide for the methylation of polymer-supported phenoxides.

$$R'\overset{+}{N}R_3\ ArO^- + (MeO)_2SO_2 \longrightarrow ArOMe + R'\overset{+}{N}R_3\ MeOSO_3^-$$

The O-methylation of a number of polymer-supported phenoxides was carried out in methanol, benzene and dioxane. The yields of products and the progress of the reaction were both dependent on the nature of the solvent (Table). In methanol, all the monohydric phenols except the sterically hindered 2,6-diisopropylphenol were methylated in excellent yields and in a very short time. The effect of bulky ortho substituents on the rate of the reaction was studied with thymol and 2,6-diisopropylphenol; unfortunately, all our attempts to prepare polymer-supported 2,6-di-t-butylphenoxides failed.[3] Both thymol and diisopropylphenol could be converted to the corresponding methyl ethers in relatively good yields, although introduction of two bulky substituents led to lowered yields. Conversion of dihydric phenols took longer time, apparently because of unfavorable