

REACTION OF 4-METHYL-5,6-DIHYDRO-2H- AND
4-METHYLENETETRAHYDROPYRANS WITH
PHENYLSULFINYL CHLORIDE

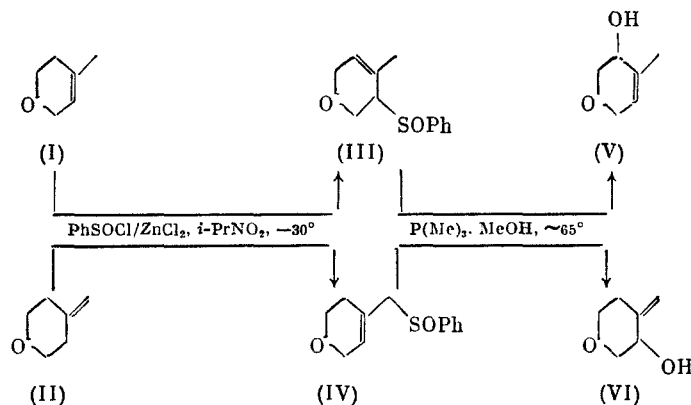
Yu. V. Pavlov, V. V. Veselovskii,
U. G. Ibatullin, and A. M. Moiseenkov

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4-Methyl-5,6-dihydro-2H- and 4-methylenetetrahydropyrans undergo an ene-type reaction with phenylsulfinyl chloride in the presence of ZnCl_2 to give the corresponding allylic sulfoxides.

Functional derivatives of commercially available unsaturated cyclic ethers (I) and (II) are promising intermediates for organic synthesis [1]. Considerable interest is found in the functionalization of heterocyclic olefins (I) and (II) using an ene-type reaction in light of the regiospecificity of the reaction of PhSOCl with linear isoprenoid olefins catalyzed by Lewis acids [2, 3].

We have found that hydropyrans (I) and (II), which were used in light of their lability in ~1.5-molar excess relative to PhSOCl and ZnCl_2 , are smoothly converted under previously described conditions [2, 3] to allylic sulfoxides (III) and (IV), respectively.



The structures of the previously unreported compounds were supported by elemental and physicochemical analysis. In particular, the PMR spectra of (IV) and (III), isolated as a mixture of approximately equal amounts of diastereomers, show olefin proton signals at 5.5-5.7 ppm. In the case of (IV), the signal for the CH_2SO protons has the form of an AB spectrum centered at δ 3.43 ppm.

Additional evidence for the structures of (III) and (IV) is found in the conversion of these compounds to the corresponding allylic alcohols (V) and (VI) using the sulfoxide-sulfonate rearrangement [4] with yields >65%; these alcohols were previously isolated in low yield from a mixture of the photooxidation products of (I) [5].

EXPERIMENTAL

The IR spectra were taken in chloroform on a UR-20 spectrometer. The PMR spectra were taken in CDCl_3 solution on a Bruker WM-250 spectrometer. The mass spectra were taken on a MAT CH-6 mass spectrometer at 70 eV.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. October Revolution Fortieth Anniversary, Bashkir State University, Ufa. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 6, pp. 1446-1447, June, 1990. Original article submitted September 18, 1989.

4-Methyl-5-phenylsulfinyl-5,6-dihydro-2H-pyran (III). A sample of 1.64 g (10.2 mmol) PhSOCl [6] was added in a single portion to a suspension of 1.36 g (10 mmol) ZnCl₂ and 1.47 g (15 mmol) (I) in 7 ml *i*-PrNO₂ stirred at -60°C in an argon atmosphere. The reaction mixture was brought to -30°C over 15 min and stirred for 1 h at this temperature. The mixture was then consecutively treated with a solution of 1.59 g (20.1 mmol) pyridine in 10 ml ether at -60°C and 10 ml water at 0°C. The aqueous layer was removed and extracted with ether. The combined organic layer was washed with water, dried over MgSO₄, and evaporated in vacuum. The residue (~2 g) was subjected to chromatography on 60 g silica gel. Gradient elution from hexane to ether gave 1.05 g (46%) (III) as a light yellow oil, *R*_f 0.51 (Silufol silica gel plates with ether as the eluent). IR spectrum (ν , cm⁻¹): 840, 910, 1005, 1050, 1090, 1110, 1135, 1145, 1210, 1240, 1260, 1280, 1295, 1390, 1450, 1480, 1590, 2830, 2890, 2920, 2975, 3070. PMR spectrum (δ , ppm): 1.98 br.s (3H, CH₃), 3.3 m (1H, CHS), 3.5-4.3 m (4H, CH₂O), 5.69 br.s (1H, HC=C), 7.4-7.6 m (5H, C₆H₅). Found: C, 64.84; H, 6.33; S, 14.23%, *M*⁺ 222. Calculated for C₁₂H₁₄O₂S: C, 64.84; H, 6.35; S, 14.42%, mol. mass 222.3.

4-Phenylsulfinylmethyl-5,6-dihydro-2H-pyran (IV). By analogy, 1.47 g (15 mmol) (II), 1.64 g (10.2 mmol) PhSOCl, and 1.36 g (10 mmol) ZnCl₂ in 7 ml *i*-PrNO₂ gave 0.87 g (38%) (IV) as colorless crystals, mp 97-99°C (CH₂Cl₂-hexane). IR spectrum (ν , cm⁻¹): 860, 980, 1035, 1060, 1090, 1130, 1245, 1380, 1450, 1670, 2835, 2860, 2930, 2975, 3065. PMR spectrum (δ , ppm): 2.1 m (2H, HC⁵), 3.43 AB (2H, CH₂S, *J*_{AB} = 20 Hz, $\Delta\delta$ 0.16), 3.75 m (2H, HC⁶), 4.11 br.s (2H, HC²), 5.54 br.s (1H, HC=C), 7.5-7.7 m (5H, C₆H₅). Found: C, 64.85; H, 6.30; S, 14.39%, *M*⁺ 222. Calculated for C₁₂H₁₄O₂S: C, 64.84; H, 6.35; S, 14.42%, mol. mass 222.3.

Dihydropyranol (V). A solution of 0.77 g (3.46 mmol) (III) and 0.86 g (6.93 mmol) P(OMe)₃ in 10 ml methanol was heated in an argon atmosphere at about 65°C for 2 h and then evaporated in vacuum. The residue (~1 g) was subjected to chromatography on 30 g silica gel. Gradient elution from hexane to 1:1 hexane-ether gave 0.27 g (68%) (V) as a colorless oil, bp 80-81°C (11 mm), *n*_D²⁰ 1.4712 [5]. The IR and PMR spectra of (V) were virtually identical to those given by Sato et al. [5].

Tetrahydropyranol (VI). By analogy, 0.77 g (3.46 mmol) (IV) gave 0.26 g (66%) (VI) as a colorless oil, bp 78-80°C (11 mm), *n*_D²⁰ 1.4658 [5]. The IR and PMR spectra of (VI) were virtually identical to those given by Sato et al. [5].

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