Chemistry of Heterocyclic Compounds, Vol. 42, No. 11, 2006

MALTOL TOSYLATE AND TRIFLATE POSSESSING NONLINEAR OPTICAL PROPERTIES

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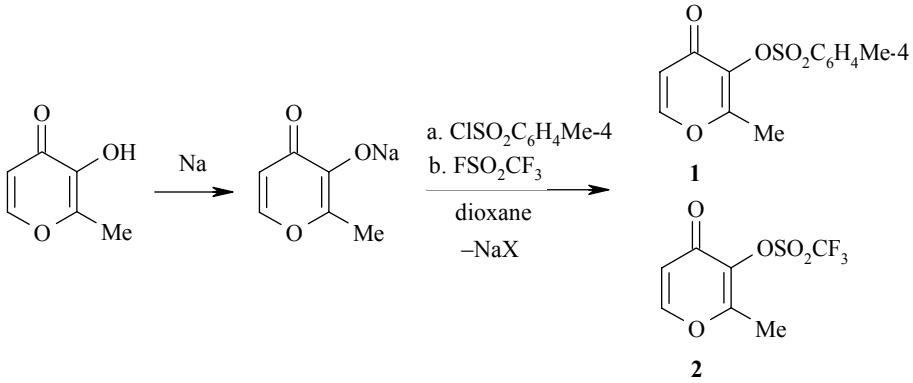
Keywords: maltol, tosylate, triflate, second harmonic laser emission, non linear optical properties.

3-Hydroxy-2-methyl-4H-pyran-4-one (maltol) has a broad spectrum of practically useful properties [1-3] and is a naturally occurring synthon [5, 6]. The subsequent functionalization of this γ-pyrone ring with highly reactive groups is a current goal.

For the first time we have shown that tosyl chloride and trifluoromethanesulfonyl fluoride react with sodium maltol (prepared from maltol and metallic sodium in absolute dioxane) to give good yields of the maltol tosylate and triflate **1** or **2** respectively.



X = F, Cl

With the use of the powder method [7] compounds **1, 2** generate a second harmonic emission of a neodymium laser with an efficiency comparable with that for the classical nonlinear optical material lithium iodate.

The chemical and nonlinear optical properties of the compounds prepared are being examined in detail.

^{1}H NMR spectra were recorded on a Bruker DPX 400 (400 MHz) spectrometer using $CDCl_3$ with HMDS as internal standard. Mass spectra were recorded on a Hewlett-Packard HP 5971A instrument (EI, 70 eV). IR spectra were taken on a Specord IR-75 spectrophotometer in the range 4000-800 cm^{-1} in KBr and on a Specord M 82 in the range 800-200 cm^{-1} using vaseline oil. Generation of the second harmonic was studied by the powder method [7] with the action of neodymium laser irradiation on yttrium aluminium garnet (YAG) at a

* Dedicated to Academician M. G. Voronkov on his 85th birthday.

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 0009-3122/06/4210-1368

wavelength of 1064 nm, working with Q switch modulation. The power density of the exciting radiation was about 10^8 watts/cm^2. The spectrum of the second harmonic irradiation for the samples investigated was recorded with an original laboratory optical spectrometer with a measurement error of less than 1 nm.

Sodium 2-methyl-4-oxo-4H-pyran-3-olate. Finely rolled metallic sodium (0.24 g, 10 mmol) was mixed with absolute dioxane (50 ml). The mixture was refluxed with vigorous stirring under an argon atmosphere in a flask fitted with reflux condenser until the metallic sodium had fully melted (20-30 min). Maltol (1.38 g, 11 mmol) was added to the suspension obtained and refluxed with constant stirring until hydrogen evolution had ceased (about 3 h).

2-Methyl-4-oxo-4H-pyran-3-yl-4-methylphenylsulfonate (1). A solution of tosyl chloride (2.0 g, 10 mmol) in dioxane (15 ml) was added dropwise to the suspension of sodium maltol cooled to 13°C. The mixture was stirred for 4-5 h at room temperature, diluted with water (1 : 1), and extracted with ether. The ether extract was evaporated to dryness and the solid residue of maltol tosylate obtained was purified by recrystallization from ethanol to give the product (2.1 g, 71.4%) with mp 110°C. IR spectrum, ν, cm^{-1}: 1640 (C=O), 1615 and 1560 (C=C), 1580 (arom.), 1350 and 1160 (S=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.97 (2H, d, *J* = 8.3, *o*-$CH_3C_6\underline{H}_4SO_2$) and 7.35 (2H, d, *J* = 8.3, *m*-$CH_3C_6\underline{H}_4SO_2$); 7.63 (1H, d, *J* = 5.8, H-5); 6.31 (1H, d, *J* = 5.8, H-6); 2.440 (3H, s, $C\underline{H}_3C_6H_4SO_2$); 2.438 (3H, s, CH_3); ^{13}C NMR spectrum, δ, ppm: 171.95 (C-4); 162.96 (C-2); 154.07 (C-6); 145.64 (CS); 138.76 ($\underline{C}_{arom}$-CH_3); 133.42 (C-3); 129.63 (*m*-$CH_3\underline{C}_6H_4SO_2$) and 128.77 (*o*-$CH_3\underline{C}_6H_4SO_2$); 117.44 (C-5); 21.83 ($\underline{C}H_3C_6H_4SO_2$); 16.10 ($CH_3$). Found, %: C 55.73; H 4.19; S 11.28. $C_{13}H_{12}SO_5$. Calculated, %: C 55.71; H 4.26; S 11.30.

2-Methyl-4-oxo-4H-pyran-3-yltrifluoromethanesulfonate (2). Trifluoromethanesulfonyl fluoride (1.58 g, 10 mmol) was passed through the sodium maltol solution in dioxane cooled to room temperature. The mixture was stirred for 40-60 min, filtered, diluted with water (1 : 1), and extracted with ether. The ether extract was evaporated to dryness to give the solid maltol triflate which was purified by sublimation at reduced pressure (28°C). The yield of pure product was 1.96 g (72.6%) with mp 44°C. IR spectrum, ν, cm^{-1}: 1657 (C=O), 1635 and 1570 (C=C), 1420 and 1125 (S=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.73 (1H, d, *J* = 5.8, H-5); 6.48 (1H, d, *J* = 5.8, H-6); 2.43 (3H, s, CH_3). ^{13}C NMR spectrum δ, ppm (*J*, Hz): 170.48 (C-4); 161.34 (C-2); 154.79 (C-6); 139.10 (C-3); 117.33 (C-5); 123.27-116.90 (dd, *J* = 320, CF_3); 15.55 (CH_3). Mass spectrum, *m/z* (I_{rel}, %): 258 $[M]^+$ (22), 189 $[M\text{-}CF_3]^+$ (1), 174 $[M\text{-}CF_3\text{-}CH_3]^+$ (5), 125 $[M\text{-}SO_2CF_3]^+$ (12), 109 $[M\text{-}OSO_2CF_3]^+$ (1), 97 (26), 80 $[OSO_2]^+$ (8), 71 (6), 69 $[CF_3]^+$ (21), 54 (11), 43 (100). Found, %: C 32.64; H 2.36; F 22.31; S 12.52. $C_7H_5F_3SO_5$. Calculated, %: C 32.56; H 1.94; F 22.09, S 12.40.

This work was supported by the Russian Fund for Basic Research (grants 05-03-97208 and 05-04-97269).

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