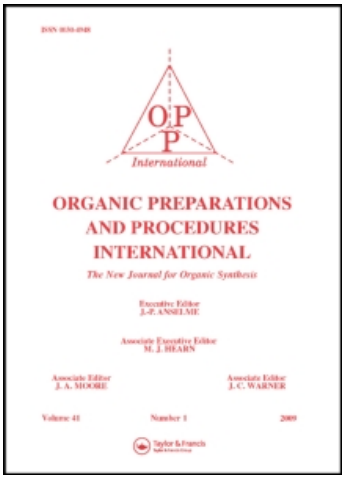

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PREPARATION OF 2, 6-DIMETHYL-4-PHENYLPYRYLIUM SULFOACETATE

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PREPARATION OF 2,6-DIMETHYL-4-PHENYLPYRYLIUM SULFOACETATE

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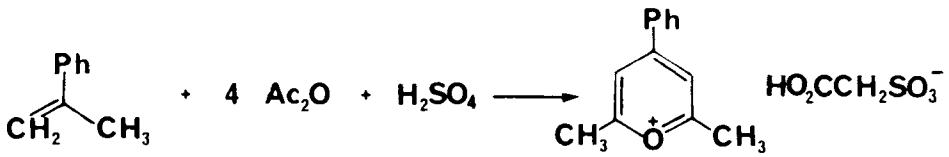
Although pyrylium salts are valuable intermediates in the synthesis of various carbocyclic and heterocyclic compounds,[1] only a few preparative methods are described in detail and these are limited to the commercially available 2,4,6-trimethylpyrylium[2,3] and 2,4,6-triphenylpyrylium[4] salts. Some of these methods are based on the diacylation of alkenes or of alkene precursors[5] and all except the ones described in the present Journal,[3,4]

give either the expensive fluoroborates and trifluoromethanesulfonates or the relatively hazardous perchlorates. The present Brief describes a simple method for the preparation of the title compound in which the sulfoacetate anion, beside being cheap and non-explosive, confers to this synthetically useful pyrylium salt an increased solubility in protic solvents, as indicated by the measured data.[6]



α-Methylstyrene was diacylated by acetic anhydride in the presence of sulfoacetic acid to afford the stable and highly water-soluble 2,6-dimethyl-4-phenylpyrylium sulfoacetate in 25-30% yield; this low yield is acceptable taking into account the availability of the starting materials. The method is an adaptation of the preparation of 2,4,6-trimethylpyrylium sulfoacetate.[3] Anions other than sulfoacetate (e.g. perchlorate, iodide, tetrafluoroborate, chloroferrate, etc.) can be readily exchanged by treatment of a concentrated aqueous solution of the sulfoacetate with the respective concentrated acid, followed by collection on a frit.

EXPERIMENTAL SECTION

2,6-Dimethyl-4-phenylpyrylium Sulfoacetate.- In a two-liter four-necked flask equipped with a mechanical stirrer, reflux condenser, dropping funnel and thermometer, sulfoacetic acid was prepared by the dropwise addition of 81 ml (149 g, 1.52 mol) of conc. sulfuric acid to 1000 ml (1090 g, 10.7 mol) of acetic anhydride and allowing the temperature to rise to 60° (gentle external heating is required). The flask was kept at 60° for 30 min. after completion of the addition. The yellow mixture was then heated to 80° (the color turns orange) and freshly distilled α-methylstyrene (198 ml, 180 g, 1.52 mol) was added dropwise without

external heating but maintaining the reaction temperature at 80°. After addition of the first drops, the mixture darkened completely. The addition required about 100 min. after which the mixture was stirred at 75° for 60 min., allowed to cool to 40° and then it was poured into 5 liters of dry acetone. The product crystallized overnight (storage in an ice box, scratching or seeding with crystals from a previous run, are helpful) forming a solid crust of brown crystals. Decantation, filtration and four washings with acetone after grinding the crystals in a mortar afforded 123 g of crude product melting at 170-174° (25% yield based on α-methylstyrene). One recrystallization from isopropanol-acetic acid (3:1 by volume) after boiling with charcoal gives brick-red needles of mp. 175-177°. Optionally, addition of the acetone washings (ca. 500 ml) to the mother liquor afforded after refrigeration a second crop of about 20 g of crude sulfoacetate, increasing the yield to about 30%. From filtrates of recrystallization procedures, the pyrylium cation may be precipitated as tetrafluoroborate or perchlorate.

A second recrystallization of the sulfoacetate from isopropanol gave an analytical sample, mp. 178°. ^{1}H-NMR (CF_3COOH): δ 3.04 (s, 6H, 2- and 6-CH_3), 4.33 (s, 2H, $\underline{CH_2}$-COOH), 7.72-7.87 (m, 3H, 3'-, 4'- and 5'-phenyl-H), 8.03-8.20 (m, 2H, 2'- and 6'-phenyl-H), 8.20 (s, 2H, 3- and 5-H); IR (KBr): 616(ms), 687(m), 790(ms), 1037(vs), 1529(s), 1585(m), 1635(s), 1718(s) cm^{-1}; UV (H_2O), λ_{max}, nm (log ε): 212(3.62), 227(3.74), 293(4.16), 416(1.86).

Anal. Calcd. for $C_{15}H_{16}O_6S$: C, 55.55; H, 4.97; S, 9.88

Found: C, 55.72; H, 5.15; S, 9.65

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6. Solubilities of the sulfoacetate in various solvents (g in 100 ml solution) at 20° are: water, 55*; acetic acid, 13; methanol, 7.5; acetone, 0.2*; values marked with asterisk have larger relative errors.