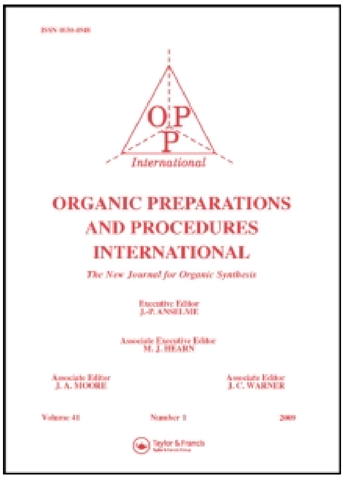

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2,4,6-TRIPHENYLPYRYLIUM HYDROGEN SULFATE

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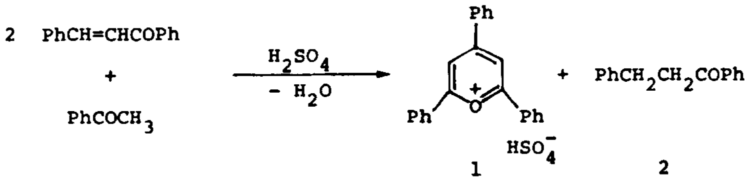
We report a simple, rapid, and high-yield one-pot synthesis of a new 2,4,6-triphenylpyrylium salt (1). Acetophenone and chalcone were condensed by Michael addition in the presence of sulfuric acid to afford 1,3,5-triphenyl-1,5-pentanedione, which is dehydrogenated *in situ* by the conjugate acid of a second chalcone molecule to yield the saturated monoketone 2 and the conjugate acid of the dione; the latter cyclizes with dehydration to yield the pyrylium cation.



1 2

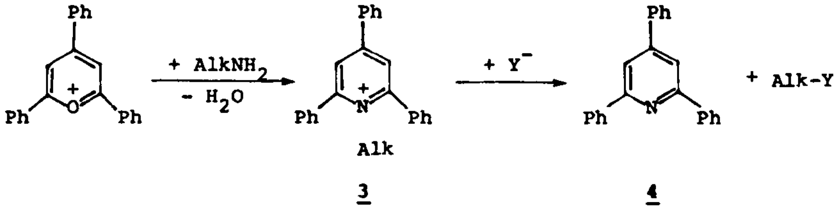
The dehydrogenation by means of chalcone in the above reaction was demonstrated in 1963 by using either 96% sulfuric or 70% perchloric acid, but in both cases the pyrylium salt was isolated as perchlorate.[1a] The present paper reports that with the use of sulfuric acid, treatment of the reaction mixture with acetone and collection of the crystalline salt, removes all unreacted starting materials together with 2 and other by-products, leaving 2,4,6-triphenylpyrylium hydrogen sulfate (1) in 80-82% yield. This salt is fairly soluble in ethanol (4.3%), water (1.3%) and acetic acid, less soluble in dichloromethane (0.3%) and practically insoluble (0.04%) in acetone at 20°, unlike the corresponding perchlorate or fluoroborate which are insoluble in water and only sparingly soluble in ethanol, acetic acid or dichloromethane.

The same type of work-up using acetone had enabled us to obtain 2,4,6-trimethylpyrylium sulfoacetate.[2] Dimroth et al.[3] adapted the reaction between acetophenone and two moles of chalcone for the preparation of 2,4,6-triphenylpyrylium tetrafluoroborate, but the procedure requires ethereal fluoroboric acid which must be prepared from boron trifluoride etherate in Teflon containers and the yield is only about 65%.

2,4,6-Triphenylpyrylium salts are useful as starting materials in many reactions,[4-6] e. g. with ammonia at 78-100° to give 2,4,6-triphenylpyridine via an intermediate which dehydrates readily,[7] with phenylhydrazine to yield 3,5-diphenyl-5-phenacyl-2-pyrazoline,[8] with hydroxylamine to form an analogous isoxazoline,[8] with hydrazine to form 3,5,7-triphenyl-4H-1,2-diazepine,[8] with nitromethane to afford 2,4,6-triphenylnitrobenzene[9] (and hence 2,4,6-triphenylaniline,[10] 2,4,6-triphenylphenol,[10] and 2,4,6-triphenylphenoxyl[10]), or with aqueous bases ($NaHCO_3$, NaOAc)[11] to yield the crystalline 1,3,5-triphenylpentene-1,5-dione which cyclizes with strong acids reforming pyrylium salts (this allows anion exchange reactions, e. g. replacement with halide ions such as I^- with aqueous-ethanolic hydriodic acid, or HCl_2^- with gaseous HCl in benzene).[1b]

One of the most interesting synthetic applications of pyrylium salts involves their reaction with primary aliphatic amines leading to N-alkyl-2,4,6-triphenylpyridinium cations (3). It had been reported in 1969 that such cations readily undergo alkyl-nitrogen bond fission by nucleophilic attack.[12] During recent years, Katritzky and coworkers[13] have shown that conversion of primary amines into pyridinium salts 3 followed by reaction with a host of nucleophiles (Y = Hal, OH, OR, OCOR, SR, SCN, N_3, PPh_3, $RCHNO_2$, NO_3, $ArSO_2$, etc.) allows the conversion of amines Alk-NH_2 into various derivatives Alk-Y, taking advantage of the fact that 2,4,6-triphenylpyridine (4) is an excellent leaving group. In some cases, conversion of primary amines into 3 followed by thermolysis is preferable to the Hofmann degradation via exhaustive methylation to give alkenes.

The readily soluble triphenylpyrylium salt reported in the present paper will be useful in connection with the above reactions developed by Katritzky; after formation of the hydrogen sulfate 3, this soluble intermediate should not be isolated but converted directly into Alk-Y. When using 1 with expensive primary amines to form 3, instead of the usual[13] reaction conditions, it may be useful to add a tertiary amine (possibly the non-nucleophilic sterically hindered 2,6-di-t-butyl-4-methylpyridine[14]) to neutralize the acid and thus improve the yield relative to amine.



EXPERIMENTAL SECTION

In a two-liter flask fitted with a stirrer, an immersion thermometer, a reflux condenser and a dropping funnel, 208 g (1 mole) of chalcone and 58 ml (60 g, 0.5 mol) of acetophenone were heated on the water bath at 60° until a homogeneous mixture was formed. Then the water bath was removed and 57 ml (104 g, 1 mole) of 96% sulfuric acid were added dropwise under stirring without external heating so that the temperature of the viscous mixture reached 125-130° and stayed at this temperature. After completion of the addition, stirring was continued for 15 min. at 125-130° and then until the temperature dropped to 60-65°, at which time acetone (1 l.) was added cautiously through the condenser. The mixture was stirred for 30 min. until it cooled to room temperature; the crystals of 1 were collected, washed thoroughly on the Buchner funnel with acetone, and left to dry in the air. The crude yellow product, 160-165 g (80-82%), mp. about 240°, is convenient for most purposes. A pure product, mp. 266-268°, is obtained by recrystallization from ethanol.

Anal. Calcd. for $C_{23}H_{18}O_5S$: C, 67.97; H, 4.46; S, 7.89

Found: C, 67.70; H, 4.17; S, 7.64

The ^{1}H-NMR (in CF_3CO_2H)[15] and IR spectra (in KBr pellet)[16] agree with published literature data for 2,4,6-triphenylpyrylium perchlorate.

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