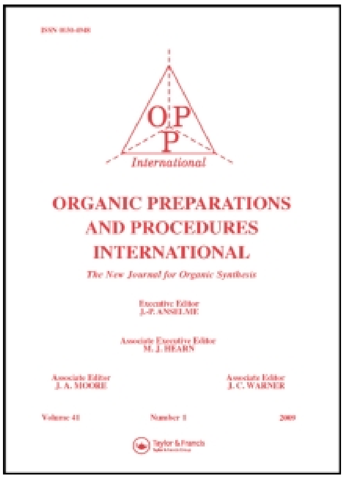

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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Alexandru T. Balaban[a]
[a] Organic Chemistry Department, The Polytechnic, Bucharest, RUMANIA

To cite this Article Balaban, Alexandru T.(1977) 'IMPROVED SYNTHESIS OF 2,6-DI-*t*-BUTYL-4-METHYLPYRYLIUM CHLOROSTANNATE AND PERCHLORATE AND OF 2,6-DI-*t*-BUTYL-4-METHYLPYRIDINE', Organic Preparations and Procedures International, 9: 3, 125 — 130

To link to this Article: DOI: 10.1080/00304947709356868

URL: http://dx.doi.org/10.1080/00304947709356868

ORGANIC PREPARATIONS AND PROCEDURES INT. 9(3), 125-130 (1977)

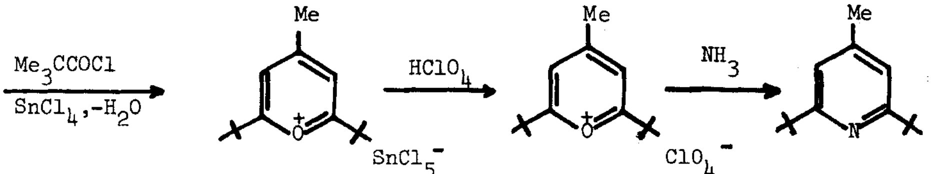
IMPROVED SYNTHESIS OF 2,6-DI-t-BUTYL-4-METHYLPYRYLIUM CHLOROSTANNATE AND PERCHLORATE AND OF 2,6-DI-t-BUTYL-4-METHYLPYRIDINE

Alexandru T. Balaban

Organic Chemistry Department, The Polytechnic, Bucharest, RUMANIA

Diacylation of isobutene with pivaloyl chloride was shown to yield 2,6-di-t-butyl-4-methylpyrylium salts I and II.[1] The olefin can be generated *in situ* from t-butyl chloride when the catalyst and anion-forming reagent is tin tetrachloride,[1] or from t-butanol when it is trifluoromethane sulfonic acid (triflic acid);[2] in the latter case, we found that replacement of t-butanol by t-butyl chloride lowered the yield considerably.

$$Me_3CCl \xrightarrow{-HCl} Me_2C{=}CH_2 \xrightarrow[-HCl]{Me_3CCOCl} Me_2C{=}CHCOCMe_3$$



I II III

Salts I and II react[2] with ammonia to yield 2,6-di-t-butyl-4-methylpyridine (III), a non-nucleophilic base.[3,4]

The present paper reports the preparation of the title compounds starting from t-butyl chloride, pivaloyl chloride and tin tetrachloride (the latter is less expensive than triflic acid); we used a modification of the initial procedure[1] by making use of the observation that liquid complexes are formed between some pyrylium salts and benzene. These complexes are probably donor-acceptor complexes. They are poorly miscible with water and benzene, so that three liquid phases result, which can be conveniently separated in a separatory funnel. This formation of three immiscible liquid phases is an unusual phenomenon, seldom encountered when none of the phases is a liquid metal. The formation of such complexes had been observed earlier.[5] Treatment of the crystalline 2,4,6-trimethylpyrylium tetrachloroferrate with excess benzene, yields two liquid phases; the complex, constituting the lower phase, was now found to contain four moles of benzene per mole of pyrylium salt (by weight difference before and after evaporation of the benzene from the separated lower phase, since ^{1}H-NMR spectra cannot be used for the paramagnetic chloroferrate). In the present case, ^{1}H-NMR spectroscopy indicated that it contains 2.3 moles of benzene per mole of pyrylium chlorostannate I.

EXPERIMENTAL

2,6-Di-*t*-butyl-4-methylpyrylium chlorostannate (I).- In a 1 ℓ. round-bottom flask containing a few boiling chips, connected to a short reflux condenser protected from atmospheric moisture by a down-turned calcium chloride tube, 92 g (105 ml, 1 mole) of *t*-butyl chloride,[6] 240 g (235 ml, 2 moles) of pivaloyl chloride,[7-9] and 261 g (118 ml, 1 mole) of tin tetrachloride were mixed at room temperature. The reaction was started by brief warming to 45-50° and evolution of hydrogen chloride was observed. The flask was left at room temperature for 36-50 hrs, until the evolution of HCl subsided and the mixture formed large crystals of chlorostannate I. This chlorstannate may be isolated by filtration with suction with a coarse or medium-porosity glass fritted funnel; the suction flask is changed and the product was washed with three 50-ml portions of benzene. The filtrate and benzene washings were worked up separately, as described below. The non-hygroscopic crystals of 2,6-di-t-butyl-4-methylpyrylium chlorostannate were air-dried to yield 75 g (15%) of I, mp. 118-120°. Its elemental analysis (without purification) showed that it is not a hexachlorostannate $(C_{14}H_{23}O^+)_2\ SnCl_6^{2-}$ but a pentachlorostannate: $C_{14}H_{23}O^+\ SnCl_5^-$. The elemental analysis (without purification) agrees better with $C_{14}H_{23}Cl_5SOn$ than $(C_{14}H_{23}O)_2\ SnCl_6$.

Anal.Calcd for $C_{14}H_{23}Cl_5OSn$: C, 33.4; H, 4.6; Cl, 35.2; Sn, 23.6.
Found: C, 32.1; H, 5.0; Cl, 34.1; Sn, 20.6.

I can be dissolved in hot dilute hydrochloric acid, but does not crystallize on cooling; the aqueous solution precipitates the perchlorate II on treatment with perchloric acid. A crystalline product is obtained from I on recrystallization from a small amount of hot acetic acid, but the product is hygroscopic, and its elemental analysis and ^{1}H-NMR spectra reveal that an acetoxy group has replaced one chlorine atom bonded to Sn.

2,6-Di-t-butyl-4-methylpyrylium perchlorate (II).- Instead of being isolated as the chlorostannate I, all the pyrylium cation can be isolated as perchlorate. In the preceding preparation, the contents of the flask were not filtered but heated at 60-65° for 3 hrs.; the crystals of chlorostannate dissolved rapidly and the renewed evolution of hydrogen chloride gradually subsided. Then the warm liquid was poured into a large separatory funnel containing 500 ml water and 60 ml conc. hydrochloric acid. Hydrolysis of the hot reaction mixture was completed by vigorous shaking for a few minutes. After cooling, 200 ml of benzene were added, where upon three immiscible layers resulted. The lower aqueous layer was discarded, the middle layer (approx. 200 g) contained the complex of pyrylium chlorostannate (I) with benzene, while the upper layer had as its main constituents excess benzene and the monoacylation product, 2,2,5-trimethyl-4-hexen-3-one (in equilibrium with its isomer, 2,2,5-trimethyl-5-hexen-3-

one, which is the actual intermediate in the diacylation step).

A similar formation of three layers occurred when the filtrate from the previous preparation was heated at 60°, hydrolyzed with dilute hydrochloric acid as described above, and then, while still hot, the benzene washings were added; the middle layer was correspondingly less abundant, because part of I was removed by filtration.

The middle layer after separation was freed from benzene by acidification with 20 ml conc. hydrochloric acid and distillation under reduced pressure or by steam distillation. The residue was boiled with 900 ml of water in the presence of decolorizing carbon. The filtrate was treated with perchloric acid until the precipitation of II was complete. Renewed heating of the residue on the filter with water, followed by filtration and addition of $HClO_4$ afforded another portion of II. The colorless II was filtered and washed with water, then air dried (for safety reasons, heating should be avoided). When all the pyrylium salt is isolated as perchlorate, yields are about 33% (approx. 100 g of II). The product is pure enough for further use without recrystallization, but may be recrystallized from acetic acid and melts at 230° and explodes on heating to higher temperatures. If heat, impact, or grinding are avoided, II may be stored in dry state without danger.

^{1}H-NMR Spectra of I and II in trifluoroacetic acid showed three singlets at δ 1.60 (t-Bu, 18 H), 2.86 (Me, 3 H) and 7.85 (ring, 2 H), in agreement with the previously reported NMR spectrum in SO_2.[10] The ^{13}C-NMR spectrum of II was reported recently.[11]

2,6-Di-t-butyl-4-methylpyridine (III).- The perchlorate I (6.15 g) was added to a mixture of 30 ml aqueous ammonia and 30 ml ether, and stirred mechanically at room temperature for 15 minutes until the solid disappeared completely. The upper layer was separated, the lower layer extracted with

5 ml of ether, and the combined ethereal fraction was treated with an excess of 10% hydrochloric acid. The aqueous solution was separated, extracted once with ether, and then made alkaline with aqueous sodium hydroxide. The separated III was extracted with ether. After drying over powdered sodium hydroxide, III was distilled, preferably under reduced pressure (at normal pressure it boils at 226° but darkens on standing) to yield 3.3 g (80%) of a colorless liquid which solidified on cooling, mp. 34°.

The ^{1}H-NMR spectrum of III displayed three singlets in CS_2 at δ 1.28 (t-Bu), 2.29 (Me) and 6.80 (ring); in CF_3CO_2H (the NH^+-pyridinium cation) at δ 1.60 (t-Bu), 2.73 (Me) and 7.72 (Ar). Unlike other pyridines with smaller α-substituents,[12,13] but similarly to 2,6-diisopropyl-4-methylpyridine,[13] the ^{1}H-NMR peaks of pyridine III are not shifted by euorpium chelates.

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(Received April 26, 1977)