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Reaction of 1,1-Dibenzoyl-2,2-dimethylhydrazine with Methyl *p*-Toluenesulfonate

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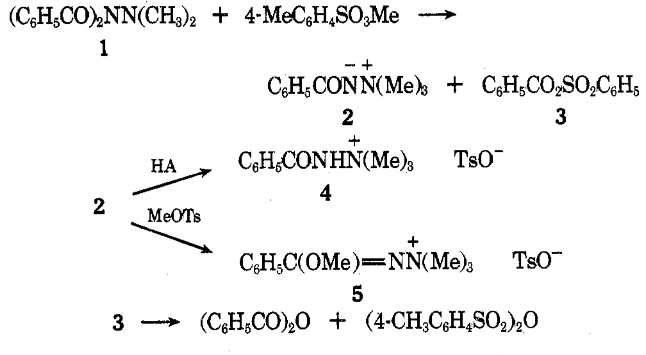
Reaction of 1,1-dibenzoyl-2,2-dimethylhydrazine with 2 equiv of methyl *p*-toluenesulfonate at 120–130 °C afforded a mixture containing 1,1,1-trimethyl-2-benzoylhydrazinium *p*-toluenesulfonate, 1,1,1-trimethyl-2-α-methoxybenzylidenehydrazinium *p*-toluenesulfonate, benzoic anhydride, and *p*-toluenesulfonic acid. The reaction apparently proceeds via the intermediate formation of 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt $[C_6H_5CO\bar{N}N^+(Me)_3]$ and benzoyl *p*-toluenesulfonate.

Hinman has reported that 1,1-dibenzoyl-2,2-dimethylhydrazine (**1**) affords debenzoylated products on reduction with lithium aluminum hydride[1] and hydrogenolysis with Raney nickel.[2] This paper reports additional examples of deacylation reactions of **1**.

We have found **1** to be unreactive to alkylation with methyl iodide but reaction with 2 equiv of methyl *p*-toluenesulfonate at 120–130 °C afforded a mixture of salts consisting of 1,1,1-trimethyl-2-benzoylhydrazinium *p*-toluenesulfonate (**4**) and 1,1,1-trimethyl-2-α-methoxybenzylidenehydrazinium *p*-toluenesulfonate (**5**). The **4**:**5** ratio varied from 0.4 to 1.5 with the O-methylated material (**5**) predominating when the reaction was conducted on a degassed reaction mixture utilizing methyl *p*-toluenesulfonate that had been freed of acid impurities. Nonionic products were found to consist of benzoic anhydride and *p*-toluenesulfonic acid. Ethyl benzoate and benzoic acid (probably originating from benzoic anhydride) were also isolated when the reaction mixture was worked up in ethanol.

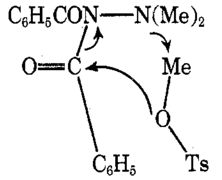
The structure of salt **5** was established by its synthesis from the reaction of 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt (**2**) with methyl *p*-toluenesulfonate.[3] Salt **4** was recovered unchanged after prolonged treatment with methyl *p*-toluenesulfonate at 120 °C.

The above results suggest that reaction of **1** and methyl *p*-toluenesulfonate initially affords 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt (**2**) and benzoyl *p*-toluenesulfonate (**3**). Once formed, **2** may then competitively undergo either O-methylation to give **5** or protonation (most likely by *p*-toluenesulfonic acid) to give **4**. The mixed anhydride (**3**) was prepared by the method of Overberger and Sarlo[4] and was found to be thermally unstable. When heated at 120 °C **3** was transformed to benzoic anhydride and *p*-toluenesulfonic acid, which are products also isolated from the reaction of **1** and methyl *p*-toluenesulfonate. The latter results may be accounted for by disproportionation[5] of **3** to *p*-toluenesulfonic anhydride and benzoic anhydride followed by selective hydrolysis of *p*-toluenesulfonic anhydride by moisture.[6]



$$\begin{aligned}
&\underset{\mathbf{1}}{(C_6H_5CO)_2NN(CH_3)_2} + 4\text{-}MeC_6H_4SO_3Me \longrightarrow \underset{\mathbf{2}}{C_6H_5CO\overset{-}{N}\overset{+}{N}(Me)_3} + \underset{\mathbf{3}}{C_6H_5CO_2SO_2C_6H_5}\\
&\mathbf{2} \xrightarrow{HA} \underset{\mathbf{4}}{C_6H_5CONH\overset{+}{N}(Me)_3}\quad TsO^-\\
&\mathbf{2} \xrightarrow{MeOTs} \underset{\mathbf{5}}{C_6H_5C(OMe){=}N\overset{+}{N}(Me)_3}\quad TsO^-\\
&\mathbf{3} \longrightarrow (C_6H_5CO)_2O + (4\text{-}CH_3C_6H_4SO_2)_2O
\end{aligned}$$

We have been unable to isolate the aminimide **2** from a reaction involving molar equivalents of **1** and methyl *p*-toluenesulfonate. The latter experiment afforded a mixture consisting of 30% of **5** and 13% of **4** (based on recovered **1**). Thus, the evidence for the intermediacy of **2** must be based on the isolation of its transformation products, **4** and **5**. A possible pathway for the conversion of **1** to **2** may involve a cyclic transition state in which N-methylation and debenzoylation occur in a concerted manner as indicated below.



We have also found that **1** is converted to *n*-butyl benzoate (54%) and 1,1-dimethyl-2-benzoylhydrazine in refluxing 1-butanol.[7]

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. NMR spectra were determined on a Perkin-Elmer R-20 spectrometer utilizing hexamethyldisiloxane as an internal standard.

Reaction of 1,1-Dibenzoyl-2,2-dimethylhydrazine (1) with Methyl *p*-Toluenesulfonate. Identification of 1,1,1-Trimethyl-

2-benzoylhydrazinium *p*-Toluenesulfonate (4) and 1,1,1-Trimethyl-2-α-methoxybenzylidenehydrazinium Tosylate (5). An ether solution of methyl *p*-toluenesulfonate was washed with several portions of 10% Na_2CO_3 solution and then dried over $MgSO_4$. A 10% methanolic solution of the ester treated as described above had pH 7.2. The base-treated ester (16.01 g, 0.086 mol) was added to 11.43 g (0.043 mol) of 1,1-dibenzoyl-2,2-dimethylhydrazine (1).[8] The mixture was frozen in liquid nitrogen, evacuated on a mercury diffusion pump, sealed, and heated at 128 °C for 12 h. The dark mixture was added with stirring to 1 l. of dry ether. The ether-insoluble material was dissolved in 50 ml of warm absolute ethanol, decolorized with Darco, and diluted with 600 ml of dry ether. Filtration of the insoluble material afforded 9.98 g of a mixture consisting of 70% of **5** and 30% of **4**, mp 106–109 °C. The composition of the mixture was obtained by comparison of the integrated intensity ratios of the –OMe NMR signal of **5** with the *p*-methyl signal of the *p*-toluenesulfonate ion. The $(Me)_3N^+$ signal of **4** appeared as a sharp side peak (δ 3.82) on the $(Me)_3N^+$ signal of **5**.

The salts were efficiently separated by fractional crystallization. In a separate experiment utilizing 10.0 g of **1** and 14 g of unwashed methyl *p*-toluenesulfonate, the ether-insoluble material was dissolved in 50 ml of absolute ethanol, decolorized, and treated with 100 ml of dry ether. Crude **4** (3.52 g) precipitated as white crystals, mp 171–174 °C. Recrystallization from ethanol–ether afforded white crystals, mp 180–181 °C (lit.[9] mp 179–181 °C). Identity was established by elemental analysis and comparison of the NMR and ir spectra with those of an authentic sample.

The filtrate from the isolation of **4** was diluted with 800 ml of anhydrous ether. The crude methoxy compound (**5**) precipitated as a hygroscopic solid (2.3 g). Recrystallization from ethanol–ether gave white crystals: mp 127–128 °C; NMR ($CDCl_3$) δ 2.20 (s, 3), 3.34 (s, 3), 3.90 (s, 9), 6.95–7.68 (m, 9).

Anal. Calcd for $C_{18}H_{24}N_2O_4S$: C, 59.31; H, 6.64; N, 7.68; S, 8.80; MeO, 8.51. Found: C, 59.15; H, 6.48; N, 7.50; S, 8.78; MeO, 8.25.

The salt obtained above was identical (ir, NMR) with **5** obtained by the following procedure. A mixture consisting of 2.0 g of 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt (**2**)[10] and 2.2 g of methyl *p*-toluenesulfonate was heated for 2 h at 120 °C. Dilution with ether gave crude **5** (2.8 g), mp 122–125 °C.

Identification of Nonionic Components. In a separate reaction (17.0 g of methyl *p*-toluenesulfonate, 12.1 g of **1**, heated for 12 h at 123 °C in an N_2 atmosphere), the filtrate remaining after precipitation of **4** and **5** from ethanol–ether as described above was evaporated to a liquid (9.3 g).

The above mixture was dissolved in 50 ml of chloroform and extracted with two 10-ml portions of 10% Na_2CO_3 solution. Acidification of the aqueous solution afforded 0.6 g of crude benzoic acid (by ir), mp 116–120 °C.

The presence of ethyl benzoate in the liquid mixture remaining after evaporation of the chloroform extracts was demonstrated by NMR and GLC retention time. Distillation of 5.23 g of the mixture afforded 0.8 g of pure ethyl benzoate (by NMR and ir), bp 44 °C (0.25 mm).

A solution consisting of 2.0 g of the crude liquid mixture (obtained from a separate experiment) dissolved in 12 ml of chloroform was extracted with two 10-ml portions of water. Evaporation of the aqueous extract afforded 0.64 g of semisolid hydrated *p*-toluenesulfonic acid which was identified by its ir and NMR spectra.

The ether-soluble material (6.65 g) from the above reaction was found to consist of a mixture of starting materials (by NMR) and benzoic anhydride. The presence of benzoic anhydride was demonstrated by its R_f value (TLC on silica gel, developing solvent benzene), by hydrolysis to benzoic acid, and by the following procedure. The mixture (6.5 g) was stirred with 20 ml of 10% NaOH for 4 h. The aqueous solution was extracted with chloroform and acidified to precipitate 1.86 g of crude benzoic acid (by ir), mp 97–98 °C. No benzoic acid could be detected (by TLC) prior to hydrolysis.

Thermal Decomposition of Benzoyl *p*-Toluenesulfonate (3). The crude anhydride (2.0 g) was heated at 124 °C for 12 h in a tube that was purged with nitrogen and stoppered. The dark, tarry residue was treated with chloroform. The chloroform-insoluble material was found to consist mainly of crude hydrated *p*-toluenesulfonic acid (by NMR and ir). Several minor impurity peaks were noted in the NMR spectrum (Me_2SO-d_6). The chloroform-soluble material was established to be benzoic anhydride (by NMR and ir) which was contaminated with a small amount of *p*-toluenesulfonic acid.

Reaction of 1,1-Dibenzoyl-2,2-dimethylhydrazine (1) with 1-Butanol. A solution containing 10 g of **1** in 50 ml of 1-butanol was heated under reflux for 12 h. After removal of the excess 1-butanol by distillation at reduced pressure, the residue was extracted with water (4 × 20 ml). The water-insoluble material was diluted with ether and dried ($MgSO_4$). Vacuum distillation of the ether-soluble residue afforded 3.6 g (54%) of pure *n*-butyl benzoate (by ir), bp 132–133 °C (22 mm). Evaporation of the aqueous washings gave a quantitative yield of 1,1-dimethyl-2-benzoylhydrazine (by ir), mp 104–106 °C (lit.[8] mp 106–107 °C).

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Registry No.—**1**, 30859-86-0; **3**, 4972-24-1; **4**, 3237-92-1; **5**, 58426-21-4; methyl *p*-toluenesulfonate, 80-48-8; 1-butanol, 71-36-3; *n*-butyl benzoate, 136-60-7; 1,1-dimethyl-2-benzoylhydrazine, 1128-86-5.

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