Reductive Dimerization of 1,3,4,6-Tetramethyl-2-phenylpyrimidinium Bistetrafluoborate

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The diquaternary salt, 1,3,4,6-tetramethyl-2-phenylpyrimidinium bistetrafluoborate (**3**) was found to undergo reductive dimerization in the presence of zinc to afford the diquaternary salt **6**.

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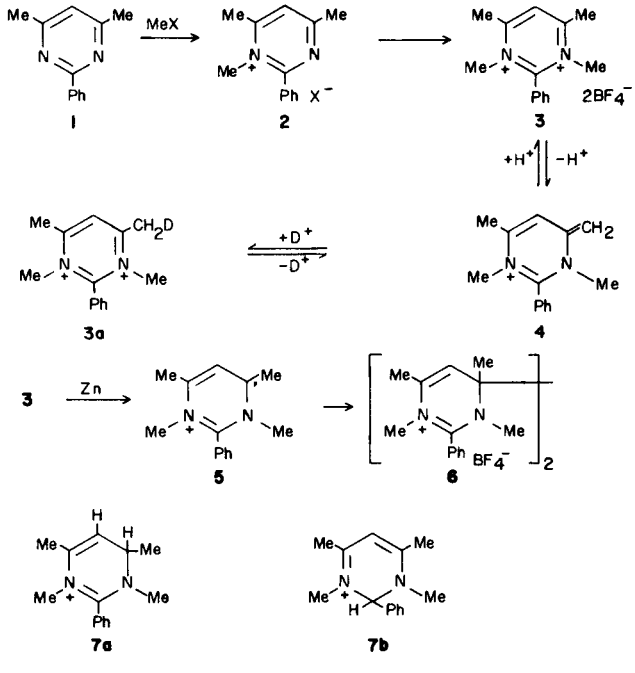
In the course of studies directed toward the synthesis of pyrimidinium ylides, we had occasion to synthesize a diquaternary salt of 4,6-dimethyl-2-phenylpyrimidine (**1**) and to investigate its behaviour in the presence of various reducing agents. We wish to report this synthesis and the interesting reductive dimerization of the diquat **3**.

The reaction of pyrimidine **1** with methyl *p*-toluenesulfonate to give monoquat **2** (X = $TosO^-$) has been reported (1); however, our efforts to prepare diquat **3** by further methylation with this reagent failed. Furthermore, reaction of pyrimidine **1** with the more potent methylating agent, methyl fluorosulfonate (2), also gave monoquat **2** (X^- = SO_3F^-), presumably because of its low solubility in the reaction medium. The best method for preparing the monoquat was to allow equimolar quantities of pyrimidine **1** and methyl fluorosulfonate to react in ether at room temperature; the monoquat precipipated in high yield and was quite pure.

In 1972, Curphey and Prasad (3) reported that a number of diazines, including some pyrimidines, could be diquaternarized using trialkyloxonium tetrafluoroborates. We found that solid pyrimidine **1** did indeed react smoothly as a partial melt with solid trimethyloxonium tetrafluoroborate at 80-100° to yield diquat **3**. It is stable for only a few days at room temperature, even in the absence of air and moisture; furthermore, it turns scarlet as it melts, the same behaviour reported by Curphey and Prasad for their pyrimidinium diquats. The *N*-methyl groups in **3** appear as a singlet at δ 4.22 in the nmr spectrum. We also observed that the singlet at δ 3.27 due to the 4- and 6-methyl groups gradually disappeared over a period of several days. This can only be explained in terms of deuterium exchange (*e.g.*, **3a**) with solvent (deuteriotrifluoroacetic acid) via intermediate **4**. Also worth noting in this series of pyrimidines, is the progressive downfield shift of 5-H as positive charge is introduced into the ring: δ 6.65 (**1**), 7.63 (**2**), 8.70 (**3**).

Diquat **3** when dissolved in dry acetonitrile reacted with zinc dust to afford a stable white compound whose structure was shown to be that of the 4,4'-dimeric diquat **6**. Proof of structure rests upon analysis of spectral data. The 2,2'-dimer is ruled out by the non-equivalence of the 4-and 6-methyl groups (δ 2.06 and 2.33, respectively) in the nmr spectrum. Monomeric dihydropyrimidinium cations **7a** and **7b** (which could arise by two-electron transfer from zinc followed by proton transfer from either acetonitrile or adventitious moisture) can be excluded based on the mass spectrum (no peak at m/e 215) and the nmr spectrum. There is no evidence of the extra hydrogen atom in the nmr spectrum, even at 100 MHz. Furthermore, structure **7a** should show doublets for 5-H and 4-methyl, and structure **7b** should show equivalent *N*-methyl groups. The product, in fact, shows singlets for both 5-H and 4-methyl (δ 5.45 and 2.06, respectively) and two *N*-methyl singlets at δ 3.19 and 3.27. The mass spectrum of the product exhibits a molecular ion at m/e 214, that expected for the cation of diquat **6** (4). It is recognized that **6** can exist in diastereomeric forms; if diquat **6** consists of such a mixture, the 100 MHz nmr spectrum does not reveal it.

Formation of the dimeric salt quite likely arises via the intermediate radical anion **4**, the product of the one-electron reduction of diquat **3**. The esr spectrum of a radical cation of pyrimidine has been reported (5), and one-electron reductions of pyridinium salts to give dimers (6) and stable radicals (7) are well documented.



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EXPERIMENTAL

Melting points were observed on a calibrated Mel-Temp devise. Nuclear magnetic resonance spectra were obtained using a Varian A-60D spectrometer with tetramethylsilane as internal standard. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

1,4,6-Trimethyl-2-phenylpyrimidinium Fluorosulfonate (**2**).

Caution: Methyl fluorosulfonate has been reported to be very toxic; it should be used with proper precautions (8). Methyl fluorosulfonate (6.6 ml., 82 mmoles) was added dropwise to a stirred solution of 13.7 g. (74.4 mmoles) of 4,6-dimethyl-2-phenylpyrimidine (9) in 100 ml. of anhydrous diethyl ether under nitrogen at room temperature. After the addition was complete (*ca* 15 minutes) the mixture was stirred for 18 hours. The white precipitate which had formed was filtered off, washed successively with ether (2 x 25 ml.) and methylene chloride (2 x 25 ml.), and then recrystallized from dry acetonitrile to afford 18.9 g. (85%) of white prisms, m.p. 178-80°; nmr (deuteriotrifluoroacetic acid): δ 2.87 (s, 3H, 4-CH_3), 2.97 (s, 3H, 6-CH_3), 4.19 (s, 3H, 1-CH_3), 7.72 (m, 5H, -C_6H_5), and 7.87 (s, 1H, 5-H).

Anal. Calcd. for $C_{13}H_{15}FN_2O_3S$: C, 52.34; H, 5.07; F, 6.37; N, 9.39. Found: C, 52.50; H, 5.01; F, 6.32; N, 9.52.

1,3,4,6-Tetramethyl-2-phenylpyrimidinium Bistetrafluoroborate (**3**).

4,6-Dimethyl-2-phenylpyrimidine (8.0 g., 43 mmoles) and trimethyloxonium tetrafluoroborate (15.9 g., 107 mmoles) were weighed out in a glove box under argon and mixed thoroughly in a pear-shaped flask. The flask was removed from the glove box and placed in a Wood's metal bath at 90°; the reaction was allowed to proceed under argon until evolution of gas (dimethyl ether) had ceased (*ca* 45 minutes). After allowing it to cool to room temperature, the hard solid mass was carefully broken up, ground with a mortar and pestle, washed with benzene (5 x 20 ml.), and then dissolved in the minimum amount of hot acetonitrile. To this was added three volumes of 1,2-dichloroethane and the resulting precipitate was collected on a filter. Repeating this procedure twice gave 11.2 g. (61%) of white crystals, m.p. 216-18° dec.; nmr (deuteriotrifluoroacetic acid): δ 3.27 (s, 6H, 4,6-CH_3), 4.22 (s, 6H, 1,3-CH_3), 7.9 (m, 5H, -C_6H_5), and 8.71 (s, 1H, 5-H).

Anal. Calcd. for $C_{14}H_{16}B_2F_8N_2$: C, 43.34; H, 4.68; F, 39.18; N, 7.22. Found: C, 43.12; H, 4.76; F, 39.14; N, 7.22.

Reduction of Diquat **3**.

Compound **3** (2.0 g., 5.1 mmoles) was dissolved in 40 ml. of dry argon-purged acetonitrile in a 100-ml. round-bottom flask. Powdered zinc (0.67 g., 10.2 mg.-atoms) was added, and after flushing with argon, the flask was tightly stoppered. The suspension was stirred magnetically at room temperature for 14 days. After filtering off the unreacted zinc, the solvent was allowed to evaporate from the filtrate in a stream of nitrogen. The residue was redissolved in the minimum amount of hot acetonitrile; the addition of two volumes of benzene precipitated a white powder, which, after being collected on a filter, was washed repeatedly with water until the washings no longer gave a positive test for zinc ions (gray-green precipitate upon addition of potassium ferricyanide solution). The remaining solid was recrystallized from acetonitrile/benzene (1:1) to yield 0.88 g. (57%) of compound **6** as a white powder, m.p. 225-30° dec.; nmr (deuteriotrifluoroacetic acid): δ 2.06 (s, 3H, 4-CH_3), 2.33 (s, 3H, 6-CH_3), 3.19 (s, 3H, 1-CH_3 or 3-CH_3), 3.27 (s, 3H, 3-CH_3 or 1-CH_3), 5.45 (s, 1H, 5-H), and 7.8 (m, 5H, -C_6H_5); ms: (70 eV) m/e 214.

Anal. Calcd. for $C_{28}H_{36}B_2F_8N_4$: C, 55.84; H, 6.03; F, 25.24; N, 9.30. Found: C, 55.45; H, 6.09; F, 25.01; N, 9.17.

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