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# CONDENSATION OF AMMONIUM ION WITH ACETONE

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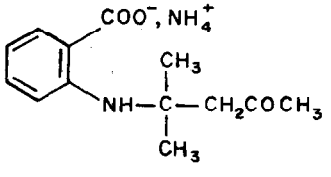
**Abstract**—Recrystallization of ammonium anthranilate or ammonium salicylate from acetone-hexane results in conversion of the ammonium salts to diacetoneammonium salts. The reaction is general for the ammonium salts of amino- and hydroxy-substituted benzoic acids, all of which are converted at least in part to diacetoneammonium salts when treated with acetone. Under similar conditions ammonium benzoate is converted to the triacetoneammonium salt. These reactions constitute convenient laboratory procedures for the preparation of diacetoneammonium and triacetoneammonium salts, and explain the frequent incursion of diacetoneamine and triacetoneamine as artifacts when natural systems are extracted with acetone.

Ammonium anthranilate, $C_7H_{10}N_2O_2$, is an easily prepared, well-behaved salt, which can be crystallized from either methanol-ether or isopropanol-hexane. It melts with decomposition at 140–143° and shows carboxylate absorption at 1520 $cm^{-1}$ (Nujol mull). When this salt is crystallized from acetone-hexane a new salt, $C_{13}H_{20}N_2O_3$, is obtained. This new product melts with decomposition at 125–126° and now shows both carboxylate absorption at 1520 $cm^{-1}$ and additional carbonyl absorption at 1712 $cm^{-1}$ (Nujol mull).

The NMR spectrum of this new salt is consistent with either structure 1 or 2.



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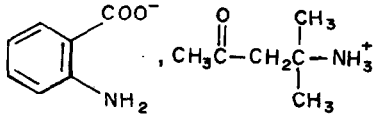

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Both possibilities represent products of condensation with acetone, with the reaction occurring on the ring amino group in 1 and on the ammonium ion in 2. Based on these structures one might expect that mesityl oxide would react more readily with ammonium anthranilate than does acetone. This did not prove to be the case, and it was not found possible to effect reaction between mesityl oxide and ammonium anthranilate.

When treated with concentrated sodium hydroxide solution this new product liberates exactly one equivalent of ammonia. But this result does not distinguish between 1 and 2, since authentic diacetoneammonium salts, e.g. diacetoneammonium trifluoroacetate, also liberate one equivalent of ammonia when treated with base. The analytical values indicated for N in the Experimental Section were obtained by the Dumas or Kjeldahl method, but the values indicated for $NH_4^+$ were obtained by alkali treatment and quantitative determination of the ammonia liberated.

For the range of reaction conditions which we explored, the condensation reaction proved to be limited to acetone. Attempts to obtain comparable reactions with butanone-2, with acetophenone or with chloral hydrate all failed.

An attempt to react sodium anthranilate with acetone was also unsuccessful and gave only the recovered sodium salt. This suggests that 2 is the correct structure for the new salt, and this hypothesis was confirmed by the results obtained when the salt was reacted with trifluoroacetic acid. The two products observed were the trifluoroacetate of anthranilic acid and diacetoneammonium trifluoroacetate. The structure of the former product was verified by its preparation from anthranilic acid and trifluoroacetic acid, and the latter product was synthesized independently by preparing diacetoneamine (2-amino-2-methyl-pentanone-4), using a modification of the procedure described by Haeseler,[1] and neutralizing it with trifluoroacetic acid.

This condensation with acetone is not unique to ammonium anthranilate. Other ammonium salts of substituted benzoic acids, to wit *p*-aminobenzoic acid, salicylic acid, *p*-hydroxybenzoic acid and *m*-hydroxybenzoic acid, form diacetoneammonium salts with acetone. Ammonium 3-hydroxy-2-naphthoate was also successfully converted to the diacetoneammonium salt, and there are indications that even simpler ammonium salts, e.g. ammonium trifluoroacetate, will condense with acetone.[2] There is one report in the literature of the successful condensation of ammonium salts of substituted benzoic acids, e.g. γ-resorcylic acid, with acetone to form diacetoneammonium salts,[3a] and salicylic acid with acetone and sodium acetate to form a triacetoneammonium salt.[3b] In the latter case no reaction

was observed in the absence of sodium acetate. In addition, salts of both diacetoneamine and triacetoneamine (2,2,6,6-tetramethyl-4-ketopiperidine) have been encountered as artifacts during extraction of natural products with acetone[4] or with acetone and ammonium iodide.[5] However, we have not tried to determine the full range of applicability of this reaction.

One might, *a priori*, expect that these acetone condensation reactions would be subject to acid-base catalysis and that the ability to effect reaction would be related in some way to the dissociation constant of the acid from which the ammonium salt was prepared. This latter expectation appears not to have been realized. Salicyclic acid ($K_a = 1.06 \times 10^{-3}$ at 25°)[6] and anthranilic acid ($K_a = 1.07 \times 10^{-5}$ at 25°)[6] differ in acid strength by two orders of magnitude, yet both ammonium salts are transformed to diacetoneammonium salts under very similar conditions. On the other hand, the ammonium salt of benzoic acid ($K_a = 6.52 \times 10^{-5}$ at 25°)[6], which has an intermediate acid strength, condenses to a different type of product, as we shall see subsequently.

The structures of the remaining diacetoneammonium salts described in this report follow from the elemental analyses, the NMR spectra and the reactions with trifluoroacetic acid. With the salts of the hydroxy-substituted benzoic acids this reaction leads to the recovered acids and diacetoneammonium trifluoroacetate. The structure of diacetoneammonium *p*-hydroxybenzoate was further confirmed by liberating diacetoneamine from diacetoneammonium trifluoroacetate and neutralizing it with *p*-hydroxybenzoic acid. The details are given in the experimental section. The $^1$H NMR spectra were usually recorded in DMSO-$d_6$ where, in addition to the aromatic protons, one observed singlets around 1.2, 2.1 and 2.7 ppm. In methanol-$d_4$ the methylene protons of diacetone-ammonium salts underwent H/D exchange with solvent which was complete in a few days.

An attempt to prepare diacetoneammonium benzoate, $C_{13}H_{19}NO_3$, by crystallizing ammonium benzoate from an acetone-containing solvent mixture led to a new condensation product, $C_{16}H_{23}NO_3$, which was shown to be triacetoneammonium benzoate. Diacetoneammonium benzoate is a stable salt, which we prepared, without difficulty, by neutralizing diacetoneamine[1] with benzoic acid. Its solubility properties are very comparable to those of triacetoneammonium benzoate. Both salts were purified by crystallization from acetonitrile. Why the reaction of the ammonium salt with acetone led to the triacetoneammonium salt in this one case is unexplained.

The structure of triacetoneammonium benzoate was verified by liberating triacetoneamine from the commercially available triacetoneammonium chloride and converting the amine to the benzoate by neutralization with benzoic acid. The $^1$H-NMR spectrum of the benzoate prepared in this manner was identical to that from ammonium benzoate and acetone, and was consistent with the proposed structure. Further proof comes from the successful conversion of the triacetoneammonium benzoate to the known chloride and the known picrate.[4]

As is apparent from our experimental section the formation of the diacetoneammonium and triacetoneammonium salts is facile even though the yields are modest. The danger of formation of diacetoneammonium and triacetoneammonium derivatives as artifacts during the extraction of natural products with acetone is, therefore, real, and acetone, in particular, and perhaps ketonic solvents, in general, should be avoided for such extractions. We would further note that the reaction of acetone with ammonium benzoate provides a convenient route to the formation of triacetoneamine (2,2,6,6-tetramethyl-4-ketopiperidine) and its salts, compounds that are not readily prepared by the standard procedure.[7]

## EXPERIMENTAL

*Ammonium anthranilate.* Technical grade anthranilic acid (69.6 g; 0.508 mole) was dissolved, with heating, in MeOH (300 ml). Conc. $NH_4OH$ (65 ml) was added to the filtered soln. The solvents were removed with the aspirator, and the crude product was crystallized from isopropanol-hexane, yielding 56.5 g (72%) of the ammonium salt; m.p. 139–143°d. A sample, recrystallized from MeOH-ether for analysis, had m.p. 140–143°d. (Found: $NH_4^+$, 11.45; N, 17.89. Calc. for $C_7H_{10}N_2O_2$: $NH_4^+$, 11.70; N, 18.17%).

*Reaction of ammonium anthranilate with acetone; diacetoneammonium anthranilate.* Ammonium anthranilate (17.6 g; 0.114 mole) was dissolved in boiling acetone (200 ml). The hot, filtered soln was treated with boiling hexane (150 ml) and cooled in the freezer to yield the diacetoneammonium salt; 12.6 g (43.9%); m.p. 95–101°d. Two recrystallizations from acetone-hexane using charcoal to decolorize gave 7 g of white solid; m.p. 125–126°d. The m.p. varied markedly with the rate of heating. $^1$H NMR (DMSO-$d_6$) $\delta$ 1.30 (s, 6, $(CH_3)_2C$), 2.12 (s, 3, $CH_3$), 2.88 (s, 2, $CH_2$), 6.48 (rough t, 1, $J \approx 8$), 6.67 (d, 1, $J \approx 8$), 7.12 (t, 1, $J \approx 8$), 7.84 (d, 1, $J \approx 8$). (Found: C, 62.59; H, 8.10; N, 11.03; $NH_4^+$, 7.01. Calc. for $C_{13}H_{20}N_2O_3$: C, 61.88; H, 7.99; N, 11.10; $NH_4^+$, 7.15%).

Diacetoneammonium anthranilate was also prepared without the intermediate isolation of the ammonium salt. The crude ammonium salt, prepared as above, was crystallized from acetone-hexane rather than isopropanol-hexane, yielding 27.6 g (21.9%) of the crude diacetoneammonium salt; m.p. 90–98°d. After two additional crystallizations from acetone-hexane the yield was 13.2 g (10.5%); m.p. 118°d. (Found: C, 62.40; H, 8.22; N(Dumas), 10.93; N(Kjeldahl), 10.75. Calc. for $C_{13}H_{20}N_2O_3$: C, 61.88; H, 7.99; N, 11.10%).

*Reaction of diacetoneammonium anthranilate with trifluoroacetic acid.* A suspension of diacetoneammonium anthranilate (10 g; 0.0396 mole) in $CHCl_3$ (250 ml) was treated with trifluoroacetic acid (15 ml; 22.3 g; 0.195 mole). A clear soln was first obtained, but this was quickly followed by the formation of a voluminous ppt. Hexane (400 ml) was added, and the mixture was cooled in the freezer. The ppt was filtered and crystallized from acetonitrile–$CHCl_3$ to yield 9.5 g (95.5%) of the trifluoroacetate of anthranilic acid; m.p. 134–135°. Recrystallization did not alter the m.p., and a mixed m.p. with the authentic trifluoroacetate of anthranilic acid (*vide infra*) showed no depression. An IR spectrum of this material was identical to that of the authentic salt. Distillation at the water pump of the combined mother liquors from the above crystallizations gave a dark oil which crystallized from $CHCl_3$–hexane to give 4.2 g (46.3%) of diacetoneammonium trifluoroacetate. Three recrystallizations from $CHCl_3$, with charcoal treatment, gave white crystals; m.p. 112–114°; undepressed on mix-melting with authentic diacetoneammonium trifluoroacetate (*vide infra*). The IR spectra of this product and the authentic salt were identical.

*The trifluoroacetate of anthranilic acid.* Anthranilic acid (8.9 g; 0.065 mole) was dissolved in boiling $CHCl_3$ (350 ml). The addition of trifluoroacetic acid (10 ml; 14.8 g; 0.13 mole) gave 16.8 g of white ppt; m.p. 134–136°. Recrystallization from acetonitrile-$CHCl_3$ gave 13.5 g (82.7%) of the salt; m.p. 134–135°.

*Diacetoneammonium trifluoroacetate.* Diacetoneamine was prepared by a modification of the procedure described by Haesler.[1] Redistilled mesityl oxide (10 g; 0.1 mole) was stirred magnetically with conc $NH_4OH$ (15 ml) with icebath cooling for 1 hr. The icebath was removed, and stirring was continued for 1.5 hr. Two layers were still present. Additional $NH_4OH$ (17 ml) was added, and stirring was continued until a single layer was present (1.3 hr). Air was bubbled through the soln for 1 hr., water was added, and the soln was extracted 3-times with ether. Trifluoroacetic acid (10 ml) was added to the ether soln, which

had been dried over $MgSO_4$. The addition of hexane, followed by cooling, gave 3.7 g (16%) of diacetoneammonium trifluoroacetate. After recrystallization from $CHCl_3$ the yield was 3.5 g; m.p. 113–114°; $^1H$ NMR (acetone-$d_6$)$\delta$1.44 (s, 6), 2.12 (s, 3), 3.0 (s, 2), 8.1 (broad s, NH). (Found: N, 6.07; $NH_4^+$, 7.81. Calc. for $C_8H_{14}F_3NO_3$: N, 6.11; $NH_4^+$, 7.87%).

*Ammonium salicylate.* Salicyclic acid (276 g; 2.0 mole) was dissolved in warm MeOH (500 ml). Conc. $NH_4OH$ (300 ml) was added with cooling, and the solvents were then removed *in vacuo*. Crystallization from isopropanol-hexane gave 262 g (84.5%) of the ammonium salt in three crops; m.p. 178–180°d.

*Reaction of ammonium salicylate with acetone; diacetoneammonium salicylate.* Ammonium salicylate (50 g; 0.322 mole) was crystallized from acetone-hexane, using as little heating as possible in dissolving the salt in the acetone. Cooling, after addition of the hexane, yielded the diacetoneammonium salt; 37.1 g (45.5%); m.p. 108–110°d. Two additional crystallizations from acetone-hexane raised the m.p. to 118–120°d; $^1H$ NMR (DMSO-$d_6$) $\delta$ 1.40 (s, 6), 2.16 (s, 3), 2.98 (s, 2), 6.8 (m, 2), 7.34 (m, 1), 7.88 (m, 1). (Found: C, 61.21; H, 7.69; N, 5.60. Calc. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53%).

*Reaction of diacetoneammonium salicylate with trifluoroacetic acid.* Diacetoneammonium salicylate (5.0 g; 0.0197 mole) was dissolved, with heating, in trifluoroacetic acid (25 ml). On cooling in the refrigerator, salicylic acid (2.3 g; 84.2%) precipitated; m.p. 155–158°. Recrystallization from water raised the m.p. to 159–160°. Addition of ether (500 ml) to the trifluoroacetic acid filtrate gave 3.1 g (68.6%) of diacetoneammonium trifluoroacetate; m.p. 113–115°. Recrystallization from acetonitrile-ether yielded 2.9 g (64.2%); m.p. 113–116°. (Found: N, 6.13. Calc. for $C_8H_{14}F_3NO_3$: N, 6.11%).

*Ammonium* p-*hydroxybenzoate. p*-Hydroxybenzoic acid (27.6 g; 0.2 mole) was dissolved in boiling MeOH (50 ml). Conc. $NH_4OH$ (25 ml) was added with icebath cooling. Addition of a large volume of ether yielded 30.2 g (97.4%) of the ammonium salt; m.p. 195–197°d.

*Reaction of ammonium* p-*hydroxybenzoate with acetone; diacetoneammonium* p-*hydroxybenzoate.* Ammonium *p*-hydroxybenzoate (5 g; 0.032 mole) was dissolved at the b.p. in a mixture of acetone (75 ml) and MeOH (50 ml). The addition of hexane (50 ml) and cooling in the freezer gave 4.6 g of the crude diacetoneammonium salt in two crops. Recrystallization from acetone-methanol-hexane gave 1.6 g (19.8%) of the salt; m.p. 135–137°d. $^1H$ NMR (DMSO-$d_6$)$\delta$1.16 (s, 6), 2.06 (s, 3), 2.62 (s, 2), 6.16 (broad s, 3), 6.60 (d, 2), 7.58 (d, 2). (Found: N, 5.49. Calc. for $C_{13}H_{19}NO_4$: N, 5.53%).

To provide proof for the structure assigned above diacetoneammonium *p*-hydroxybenzoate was also prepared as follows. Diacetoneammonium trifluoroacetate (2.0 g; 0.0087 mole) in water (10 ml) in a separatory funnel was covered with ether (50 ml). NaOH (1 g; 0.025 mole) in a minimum amount of water was added. The mixture was shaken, the ether layer was separated, and the aqueous phase was extracted two additional times with 50 ml portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered and treated with a solution of *p*-hydroxybenzoic acid (1.2 g; 0.0087 mole) in ether (50 ml). Addition of more ether and hexane gave 1.55 g (70%) of the salt; m.p. 138–140°d, after recrystallization from methanol–acetone–hexane. The IR spectrum was identical to that of the product from the reaction of ammonium *p*-hydroxybenzoate and acetone.

Treatment of diacetoneammonium *p*-hydroxybenzoate with trifluoroacetic acid by the procedure described for diacetoneammonium salicylate gave 52.4% *p*-hydroxybenzoic acid (m.p. 208–212°) and 77% diacetoneammonium trifluoroacetate; m.p. 113–114°.

*Ammonium* m-*hydroxybenzoate. m*-Hydroxybenzoic acid (13.8 g; 0.1 mole) was dissolved in boiling MeOH (25 ml) and then treated with conc. $NH_4OH$ (10 ml). After cooling to room temp., ether (200 ml) was added, yielding 15 g (96.8%) of the ammonium salt, m.p. 187–192°.

*Reaction of ammonium* m-*hydroxybenzoate with acetone; diacetoneammonium* m-*hydroxybenzoate.* Ammonium *m*-hydroxybenzoate (4.45 g; 0.0287 mole) was dissolved by boiling in MeOH (40 ml). Acetone (40 ml) was added, and the soln was boiled again for 0.5 min. Ether (100 ml) and hexane (100 ml) were added, and the soln was placed in the freezer. Although a few crystals appeared, a large additional volume of hexane was added, and the soln was returned to the freezer, where some crude product, 2.5 g (m.p. 171–181°d), precipitated. More hexane was added to the filtrate, which soln after standing several days at room temp. yielded an additional 1.8 g of crude product; m.p. 158–162°d. The two crops were combined and recrystallized from methanol–acetone–hexane to give 2.17 g (29.7%) of the diacetoneammonium salt; m.p. 171–172°d. $^1H$ NMR (DMSO-$d_6$) $\delta$ 1.18 (s, 6), 2.08 (s, 3), 2.68 (s, 2), 5.2 (broad s, 4, OH, NH) 6.5–7.3 (m, 4). (Found: N, 5.48. Calc. for $C_{13}H_{19}NO_4$: N, 5.53%).

Treatment of this salt with trifluoroacetic acid using the procedure described for diacetoneammonium salicylate gave 73.4% *m*-hydroxybenzoic acid (m.p. 199–200°) and 77.8% diacetoneammonium trifluoroacetate; m.p. 113–115°.

*Ammonium* 3-*hydroxy*-2-*naphthoate.* Conc. $NH_4OH$ (15 ml) was added to a suspension of 3-hydroxy-2-naphthoic acid (18.8 g; 0.1 mole) in MeOH (75 ml). The mixture was stirred until complete soln occurred. The solvents were removed at the water pump, and the residue was treated with ether and hexane, yielding 13.5 g (65.9%) of the ammonium salt; m.p. 212–218°d.

*Reaction of ammonium* 3-*hydroxy*-2-*naphthoate with acetone: diacetoneammonium* 3-*hydroxy*-2-*naphthoate.* The above ammonium salt (13.5 g; 0.0659 mole) was boiled with acetone (200 ml) until complete soln occurred. After filtration and cooling, ether (200 ml) and hexane (300 ml) were added. Storage in the freezer resulted in the crude product, which on crystallization from acetone-ether gave 8.7 g (43.5%) of the diacetoneammonium salt; m.p. 139–140°d; $^1H$ NMR (acetone-$d_6$) $\delta$ 1.52 (s, 6), 2.12 (s, 3), 3.06 (s, 2), 6.92 (s, 1), 7.0–7.6 (m, 4), 8.28 (s, 1). (Found N, 4.60. Calc. for $C_{17}H_{21}NO_4$: N, 4.62%).

Treatment of this diacetoneammonium salt with trifluoroacetic acid using the procedure described for the salicylate yielded 93% of 3-hydroxy-2-naphthoic acid (m.p. 225–228°) and 83% diacetoneammonium trifluoroacetate; m.p. 112–114°.

*Ammonium* p-*aminobenzoate. p*-Aminobenzoic acid (13.7 g; 0.1 mole) was suspended in warm MeOH (25 ml) and treated with conc. $NH_4OH$ (10 ml). The suspended acid went into soln immediately. The addition of a large volume of ether, after cooling to room temp., yielded 15.5 g (100%) of the ammonium salt; m.p. 165–168°d, with previous softening. (Found: $NH_4^+$, 11.83. Calc. for $C_7H_{10}N_2O_2$: $NH_4^+$, 11.70%).

*Reaction of ammonium* p-*aminobenzoate with acetone; diacetoneammonium* p-*animobenzoate.* The above ammonium salt (10 g; 0.065 mole) was dissolved by boiling with a mixture of acetone (200 ml) and MeOH (50 ml). The addition of ether (100 ml) and hexane (100 ml) did not result in crystallization. The solvents were removed at the aspirator, and the residual oil was induced to crystallize by adding acetone and ether with stirring and letting the mixture stand. A total of 11.2 g of crude product was obtained in three crops. Recrystallization from acetone-ether-hexane and then from acetone-ether yielded 3.1 g (18.9%) of the diacetoneammonium salt; m.p. 140–142°d; $^1H$ NMR (DMSO-$d_6$) $\delta$ 1.04 (s, 6), 2.02 (s, 3), 2.44 (s, 2), 3.78 (s, 5, NH), 6.34 (d, 2), 7.40 (d, 2). (Found: $NH_4^+$, 7.01. Calc. for $C_{13}H_{20}N_2O_3$: $NH_4^+$, 7.15%).

Treatment of this salt with trifluoroacetic acid, using the procedure described for diacetoneammonium anthranilate, gave 67% of the trifluoroacetate of *p*-aminobenzoic acid (m.p. 165–169°) and 68.9% of diacetoneammonium trifluoroacetate; m.p. 112–114°.

*Reaction of ammonium benzoate with acetone; triacetoneammonium benzoate.* A suspension of ammonium benzoate (5 g; 0.0359 mole) in boiling acetone (100 ml) was treated portionwise with EtOH (100 ml total) until complete soln occurred. Removal of the solvents with the water pump gave a residue which on crystallization from acetonitrile yielded 4.5 g of off-white crystals. Recrystallization from the same solvent gave 2.9 g (29.2%) of the triacetoneammonium salt; m.p. 126–129°d. A sample crystallized three additional times from acetonitrile for analysis had m.p. 131–133°d; $^1H$ NMR (DMSO-$d_6$) $\delta$ 1.12 (s, 12), 2.14 (s, 4), 4.12 (broad s, NH and $H_2O$), 7.32 (m, 3), 7.76 (m, 2). (Found: N, 5.11 Calc. for $C_{16}H_{23}NO_3$: N, 5.05%).

"*Authentic*" *triacetoneammonium benzoate.* A soln of NaOH

(4 g; 0.1 mole) in a minimum amount of water was added to triacetoneammonium chloride (3.84 g; 0.02 mole), obtained from the Aldrich Chemical Co., in water (30 ml) and ether (50 ml) in a separatory funnel. After shaking, the ether layer was separated, and the aqueous soln was extracted two additional times with 50 ml portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered, diluted with ether and treated with a soln of benzoic acid (2.44 g; 0.02 mole) in ether (50 ml). Addition of a large volume of hexane and cooling gave the crude product. After crystallization from acetonitrile the yield was 4.81 g (86.7%); m.p. 139–140°d. The IR and $^1H$ NMR spectra of this salt were identical to that of the purified product obtained from the reaction of acetone and ammonium benzoate.

Triacetoneammonium benzoate was converted to the picrate as follows. A soln of the benzoate (5 g; 0.018 mole) in boiling EtOH (50 ml) was treated with an ethanolic soln of 85% picric acid (4.85 g). Cooling in the freezer afforded 5.3 g of yellow crystals; m.p. 177–178°d after recrystallization from ethanol and drying *in vacuo* at 70°. (Found: N, 14.39. Calc. for $C_{15}H_{20}N_4O_8$: N, 14.58%).

Triacetoneammonium chloride was regenerated from the benzoate to further confirm the assigned structures. Conc. HCl (5 ml) was added to a soln of the benzoate (3 g; 0.0108 mole) in MeOH. The solvent was removed by distillation leaving a semisolid residue, which was stirred two times with ether to remove the benzoic acid; yield 1.12 g (85%) after evaporation of the ether and recrystallization from water. The ether insoluble material was crystallized from acetonitrile and yielded 1.73 g (83%) of triacetoneammonium chloride. A sample recrystallized for analysis had m.p. 196–198°d. (Found: Cl, 18.32. Calc. for $C_9H_{18}NOCl$: Cl, 18.50%).

The reaction of triacetoneammonium benzoate with triacetoneammonium chloride. A sample recrystallized for diacetoneammonium salicylate gave 73% benzoic acid and 56% triacetoneammonium trifluoroacetate; m.p. 144–146°d. A sample of the trifluoroacetate recrystallized from chloroform-hexane for analysis had m.p. 148–149°d. (Found: N, 5.16. Calc. for $C_{11}H_{18}NO_3F_3$: N, 5.20%).

Triacetoneammonium chloride was also converted to the salicylate using the procedure described for the preparation of "authentic" triacetoneammonium benzoate. The yield was 90.7% m.p. 143–144°d from ether-hexane. (Found: N, 4.73. Calc. for $C_{16}H_{23}NO_4$: N, 4.78%).

*Diacetoneammonium benzoate.* Mesityl oxide (12 ml; 10.3 g; 0.104 mole) and conc. $NH_4OH$ (30 ml) were stirred first 1 hr with icebath cooling and then overnight at room temp. Air was passed through the soln for 1.5 hr to remove ammonia. The soln was transferred to a separatory funnel and extracted with 4, 75 ml portions of ether. The ether soln was dried over $MgSO_4$, filtered and added to a soln of benzoic acid (12.2 g; 0.1 mole) in ether. Cooling gave a first crop of 12.2 g of product, m.p. 96–99°, and addition of hexane to the filtrate gave a second crop of 1.7 g, m.p. 90–98°. The total yield was 13.9 g (58.6%). Crystallization from acetonitrile raised the m.p. to 98–101°. (Found: N, 6.14. Calc. for $C_{13}H_{19}NO_3$: N, 5.90%).

The product as obtained above is contaminated with a small amount of ammonium benzoate. This can be removed by dissolving the product in hot acetonitrile, letting the ammonium benzoate crystallize at room temp., filtering and then refrigerating the filtrate to obtain the desired diacetoneammonium benzoate. After this treatment the product had m.p. 99–101° and gave 5.89% N on analysis; $^1H$ NMR (DMSO-$d_6$) $\delta$ 1.24 (s, 6), 2.06 (s, 3), 2.72 (s, 2), 5.16 (broad s, 3), 7.16 (m, 3) 7.7 (m, 2).

*Acknowledgement*—We wish to thank Dr. M. Ikawa for translations of the Japanese articles.

## REFERENCES

[1]*Organic Synthesis*, Coll. Vol. 1, p. 196. Wiley, New York (1941).
[2]Ammonium trifluoroacetate (m.p. 125–127°), crystallized from acetonehexane, refluxed in acetone-methanol and crystallized first from acetonitrile-hexane and then from chloroform after removing the acetone-methanol solvent mixture, gave slightly impure diacetoneammonium trifluoroacetate (m.p. 103–110°; no depression on mix-melting with the pure salt, m.p. 113–114°).
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