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Preparation of Tetramethylphthalimide

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Synopsis. Treatment of tetramethylphthalic anhydride (I) with 28% aqueous ammonia at room temperature afforded ammonium tetramethylphthalimide (IV) and and 2-cyano-3,4,5,6-tetramethylbenzoate (V). The amount of IV increased by heating at 100 °C, tetramethylphthalimide (VI) being precipitated. A plausible reaction path is proposed.

Of the phthalocyanine group, copper phthalocyanine is the most easily synthesized, but there is difficulty in bringing crude products into acceptable pigments, as well as in preventing a reduction of strength resulting from dispersion in vehicles.

We obtained tetramethylphthalic anhydride (I) by the hydrolysis of bis(nitromethyl)prehnitene.[1] Copper polymethylphthalocyanine synthesized from I might be expected to form more stable dispersion with vehicles, since methyl groups appear to have an affinity to them. However, when a mixture of I, urea and copper salt was heated, no copper phthalocyanine was obtained. It was obtained when tetramethylphthalimide (VI) was used instead of I.

The present study deals with the preparation of VI. We have studied the reaction of I with aqueous ammonia and found a useful procedure.

Phthalimide is formed by heating ammonium phthalate or phthalic anhydride and gaseous ammonia up to 300 °C.[2] Ammonium phthalamidate is formed by heating phthalic anhydride with aqueous ammonia, the dry salt being converted into phthalimide at about 200 °C.[3,4]

By treating I with 28% aqueous ammonia at room temperature for 5 min (Expt. No. 1), ammonium tetramethylphthalimide (IV) and 2-cyano-3,4,5,6-tetramethylbenzoate (V) were obtained in good yields, but neither tetramethylphthalate (VII) nor tetramethylphthalamidate (II) was detected. By warming, IV increased whereas V decreased (Table 1). On continued warming (Expt. No. 4), VI was obtained as a white precipitate, which may have been formed by releasing of ammonia from IV.

VI precipitated when finely powdered VI was dissolved in 28% aqueous ammonia at room temperature and the resulting clear solution was then heated at 100 °C at atmospheric pressure.

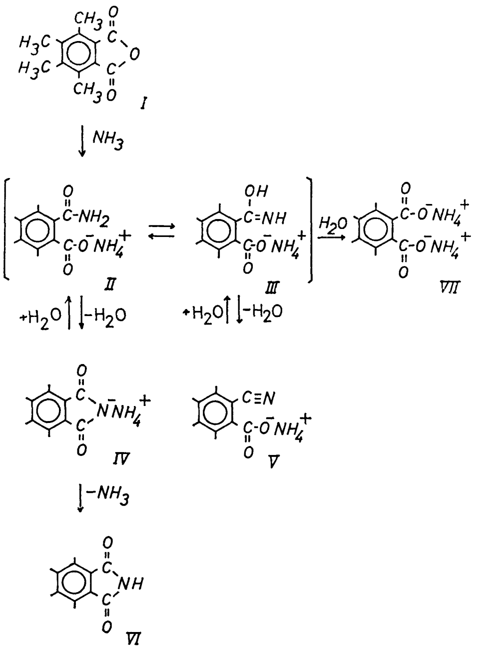
IV does not seem to be formed from ammonium tetramethylphthalate (VII) by the removal of water and ammonia, but from intermediary II. Since the repulsion of the four methyl groups on II facilitates cyclization between the amide group and the carboxyl group, IV might be formed as the cyclized product even under mild conditions, and thus II cannot be detected. VII seems to be formed by the hydrolysis of III as a minor product.

A plausible reaction path is shown in the following (Scheme 1).

Table 1. Experimental results

Expt. No.	Conditions		Products (mol %)			
	Temp.	Time	IV	V	VI[a]	VII
1	Room temp.	5 (min)	61.9	29.5	0.0	0.0
2	100(°C)	1	62.3	31.1	0.0	0.0
3	100	90	56.0	9.5	10.0	14.9
4	100	180	33.8	8.4	40.0	15.3
5	100	240	—	—	70.3	—

a) Obtained as a white precipitate.



Scheme 1.

Experimental

I was obtained by the hydrolysis of bis(nitromethyl)prehnitene, prepared by the nitration of hexamethylbenzene.[1]

Procedure. I (1.0 g) was added to 250 ml of 28% aqueous ammonia, and the mixture was stirred for a certain time at room temperature or 100 °C. Ammonia gas was allowed to escape through a reflux condenser. The color of the reaction mixture turned from opaque to clear after about 3 min even at room temperature.

Isolation of IV, V, and VII. Excess silver nitrate (100 g/ H_2O 70 ml) was added to the above solution (30 ml). The resulting precipitate was filtered off, dried, and refluxed with excess methyl iodide in benzene for 3 hr. After filtration of insoluble material, the filtrate was chromatographed on alumina, and the products were eluted with petroleum and benzene. Each fraction was evaporated and the residue was recrystallized from chloroform to give three products. The first fraction afforded *N*-methyltetramethylphthalimide (*N*-methylated VI); colorless needles, mp 180—181 °C. Found: C, 71.67; H, 7.05; N, 6.55%. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45%. IR(KBr, cm^{-1}): 1754, 1697 (C=O), 1440, 1384 (CH_3), 1253, 1105, 1003(C–N) and 757. NMR($CDCl_3$, δ ppm): 2.25 (s, $-CH_3$, 6H), 2.63 (s, $-CH_3$, 6H) and 3.08 (s, N–CH_3, 3H).

N-Methylated VI was also obtained by treatment VI with diazomethane in ether. The second fraction afforded methyl 2-cyano-3,4,5,6-tetramethylbenzoate (methylated V); colorless needles, mp 75—76 °C. Found: C, 71.73; H, 7.08; N, 6.51%. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45%. IR(KBr, cm^{-1}): 2220 ($C\equiv N$), 1732 (C=O), 1207 and 1180 (C–O–C). NMR(CCl_4, δ ppm): 2.24(s, $-CH_3$, 6H), 2.30 (s, $-CH_3$, 3H), 2.49(s, $-CH_3$, 3H) and 3.95 (s, $-OCH_3$, 3H). Colorless needles (mp 127.5—128.5 °C) were obtained from the final fraction, and identified as dimethyl tetramethylphthalate (methylated VII) by comparing the retention time in glc and IR spectrum with that of an authentic sample.[1]

These reaction products were determined by glc (column; 10% Silicone DC 550/Cellite 80—100 mesh, 4 mm × 2 m, temp; 215 °C, N_2; 40 ml/min).

Isolation of VI. 1.0 g of I was added to 250 ml of 28% aqueous ammonia, and the mixture was heated at 100 °C. The reaction mixture turned instantly from opaque to clear. On continued heating, a white precipitate was formed. After heating for 3 hr, the mixture was cooled to room temperature and the precipitate was filtered off; yield 0.4 g (40 mol% as VI). Recrystallization from methanol gave colorless needles; mp 289—290 °C. Found: C, 70.74; H, 6.32; N, 7.07%; mol wt (Rast), 206. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89%; mol wt, 203. IR(KBr, cm^{-1}): 3190 (N–H), 1752, 1696 (C=O), 1127 and 1038 (C–N). NMR (DMF-d_7, δ ppm): 2.24 (s, $-CH_3$, 6H), 2.56 (s, $-CH_3$, 6H) and *ca.* 10.7 (s, NH, 1H).

References

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