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On the Synthesis and Properties of 1-Methyl 2,6-Di-t-Butyl Pyridinium Iodine (1)

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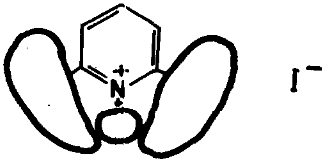
2,6-Di-t-butyl pyridine was first synthesized by Brown and Kanner(2). They showed that the compound did react with protonic acids, but did not react with Lewis acids, such as boron trifluoride, or with methyl iodide due to the steric strain of the bulky t-butyl groups.

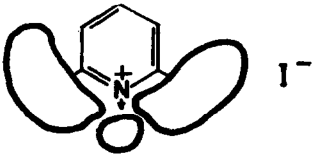
We have found that 2,6-di-t-butyl pyridine(3) reacted with methyl iodide under high pressure (~ 5000 atm.) and formed 1-methyl 2,6-di-t-butyl pyridinium iodide, m.p. 135°C, λ max 228 mμ. Product analysis were C, 50.86; H, 7.28; N, 4.25; I, 39.73. Calculated for $C_{14}H_{24}N\,I$; C, 50.45; H, 7.21; N, 4.20; I, 39.14.

1-Methyl 2,6-di-t-butyl pyridinium iodide did not react with concentrated HCl or with $NaOCH_3$ in methanol. Upon heating the compound at 250° under reduced pressure (20 mm Hg), 1-methyl 2,6-di-t-butyl pyridinium iodide was sublimed without decomposition. However, under the same conditions, 1-methyl 2,6-dimethyl pyridinium iodide was completely decomposed into 2,6-dimethyl pyridine and methyl iodide.

Possible structures of 1-methyl 2,6-di-t-butyl pyridine iodine may be I and II:



(I)



(II)

In structure I, methyl iodide reacts with the basic nitrogen and forms the usual coordination bond between nitrogen and carbon overcoming the steric hindrance of t-butyl groups; the t-butyl groups cover the methyl and acts just like the chelae of a crab. In the second structure, part of the t-butyl groups is squeezed in between the pyridyl and the methyl groups.

From the nature of structure I, it is expected that the methyl bonded with nitrogen would not be easily dissociated because of the steric hindrance of t-butyl groups. However, in structure II, there is a considerable amount of steric strain between t-butyl and methyl, and the methyl is expected to dissociate easily from the nitrogen(4).

The extraordinary stability of 1-methyl 2,6-di-t-butyl pyridinium iodide suggests that the structure of the compound is close to I. The determination of the structure will be given through x-ray analysis which is currently under investigation by Professor M. G. Rossmann at Purdue University.

References

(1) Effect of High Pressure on Organic Compounds IV. Part III. Y. Okamoto, J. Phys. Chem., in press.

(2) H.C. Brown and B. Kanner, J. Am. Chem. Soc., <u>75</u>, 3865 (1953).

(3) 2,6-di-t-butyl pyridine, b.p. 61-62°/1 mm Hg (Lit.(2) 101°/23 mm Hg) chloroaurate; m.p. 188° (Lit.(2) 184.5°). Analysis C, 29.9, H, 4.29; Cl, 26.34; N, 3.08. Calc. for $C_{13}H_{22}N$ Au Cl_4, C, 29.4; H, 4.15; Cl, 26.7; N, 2.64.

(4) H.C. Brown, J. Chem. Soc., 1248 (1956).