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STERICALLY HINDERED REACTIONS UNDER HIGH PRESSURE. REACTION OF 2,4,6-TRI-t-BUTYL N-METHYLANILINE WITH METHYLIODIDE (1)

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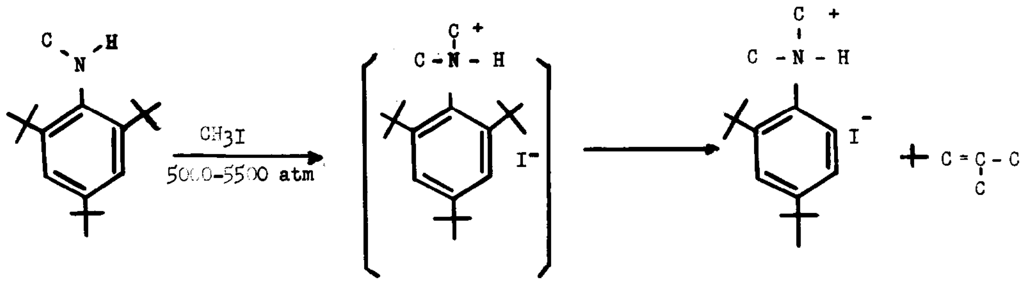
Reactions of alkyl halides with amines to form quaternary ammonium salts have been extensively investigated with respect to steric effect between reactants and the effects of pressure on the reaction (2,3). The rate of the reaction increases with increasing applied pressure on the system, and generally the greater the degree of steric hindrance present, the more pronounced the effect of applied pressure on the reaction rate.

Recently, it was demonstrated that 2,6-di-t-butyl pyridine reacts with methyl iodide only under high pressure (4). Another sterically hindered base, 2,4,6-tri-t-butyl N-methyl aniline (I) did not react with methyl iodide under conventional methods. Wepster and coworkers have attempted to prepare 2,4,6-tri-t-butyl N,N-dimethyl aniline from I by nine different methylation procedures, e.g.: I, with methyl iodide at 200°C in a sealed tube, with dimethyl sulfate at 180°C and with sodium amide-methyl iodide. However, all attempts resulted in no reaction (5).

We wish to report the effect of pressure on the reaction between I and methyl iodide. I reacted with methyl iodide under high pressure 5000-5500 atm. at 100°C in dioxane solution (or without solvent, using large excess methyl iodide) and produced

2,4-di-t-butyl N,N-dimethyl anilinium iodide (III)(yield 70%) and isobutylene (6), instead of the corresponding anilinium salt, 2,4,6-tri-t-butyl N,N-dimethyl anilinium iodide (II).



I II III

Without methyl iodide, I did not undergo de-t-butylation under these conditions. Furthermore, even when I refluxed with various concentrations of sulfuric acid or phosphoric acid under ordinary pressure, there was no de-t-butylation from I detected (5). Therefore, the de-t-butylation observed must be associated with the reaction between I and methyl iodide. Under the effect of high pressure, methyl iodide was reacted with I by overcoming the steric hindrance and the reaction intermediate may have a structure close to II.

Arnett and his coworkers (8) recently determined the strain energy of o-di-t-butyl benzene as 22.3 ± 0.5 kcal/mole which is close to Brown's estimate (25 Kcal/mole) by the homomorphic analogy (9). The presumed intermediate II is a structural homomorph of 1, 3,5-tri-t-butyl isopropyl benzene and the strain energy is expected to be more than that of O-di-t-butyl benzene. Therefore, in order to release the strain energy, the t-butyl group at the ortho position in II is readily removed to form III and isobutylene.

We are currently pursuing the mechanism of the de-t-butylation reaction as well as the effect of high pressure in other sterically hindered system.

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(6) I; nmr (CCl_4 internal TMS), δ 1.28 (singlet, nine p-t-butyl protons), δ 1.44 (singlet, eighteen o-di-t-butyl protons), δ 7.06 (singlet, two aromatic protons), δ 2.60 (three N-methyl protons). 2,4, di-t-butyl N,N-dimethyl aniline; recrystallised from 90% EtOH, m.p. 77-8°C (lit. 77-8°C) (7), nmr (CCl_4 internal TMS), δ 1.28 (singlet, nine p-t-butyl protons), δ 2.56 (singlet, six N-dimethyl protons), δ 1.40 (singlet, nine o-t-butyl protons), δ 7.12-7.24 (three aromatic protons). Isobutylene produced was qualitatively determined by a gas chromatography.

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