Solid-liquid phase transfer catalytic reaction of 1-aminoanthraquinone with alkyl halides:
A case of N-alkylation

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N-Alkylation of 1-aminoanthraquinone I has been carried out under mild condition of solid-liquid phase transfer catalysis using tetrabutyl ammonium bromide and dibenzo-(18)-crown-6 at room temperature in better yield.

Alkylation of aminoanthraquinone are valued as disperse and solvent dyes. N-Alkylation of amides under phase transfer catalysis have been described in the literature. Torossian have alkylated the amide, anilide and morfolide of phenylacetic acid under phase transfer condition and Smith described N-alkylation procedure for ethyl pyroglutamate giving the product in 80-90% yield. Zhang performed facile and convenient method for synthesis of N-aryl and N-acyl thiourea derivative under solid-liquid phase transfer catalysis conditions in high yield using polyethylene glycol. Ayyangar synthesized substituted-N-monooalkyl aromatic amines under PTC condition and suggested possible mechanism. All these methods suffered from prolong reaction time and the reaction was completed under reflux condition.

We now report herein a simple and convenient method for the preparation of monoalkylated aminoanthraquinone using combination of tetrabutyl ammonium bromide and dibenzo-(18)-crown-6 at room temperature in less time. By varying the quantity of the catalyst we observed that by taking tetrabutyl ammonium bromide (45mg) and dibenzo-(18)-crown-6 (5mg) reaction required shorter time for completion in better yield than performing the reaction with only tetrabutyl ammonium bromide or dibenzo-(18)-crown-6. Results obtained are summarized in Table I. This shows that the coordination of ion ligand cavity plays an important role in using crown ether as the effective cavity volume of the 18-membered crown ether ring which is better suited to the ion diameter of K⁺[2.66Å].

Various N-alkyl substituted aminoanthraquinone were synthesized which are summarized in Table II.

Experimental Section
Melting points were determined in open capillaries.
and are uncorrected. Purity of the compounds were checked by TLC (silica gel) and they were characterized by $^1$H-NMR and comparison with authentic samples.

**General procedure**
Alkyl halide (2a-d)/sulphate 2e (1 mmole) dissolved in 2 mL of benzene was added dropwise with efficient stirring to a mixture of 1-aminoanthraquinone (1.1 mmole), pulverized KOH (3.5 mmole), anhyd. $\text{K}_2\text{CO}_3$ (3.5 mmole), tetrabutyl ammonium bromide (45 mg) and dibenzo-(18)-crown-6 (5 mg) in 10 mL of benzene. After the completion of the reaction (monitored by TLC) the reaction mixture was filtered off to remove inorganic salt and organic layer was washed with water (3×25 mL) and dried over anhyd. Na$_2$SO$_4$. Solvent was removed by rotary evaporator and product obtained was passed through silica gel column. On eluting with pet. ether : ethyl acetate (95:5 v/v) a crystalline solid was obtained. Thus compounds 3a-e were prepared (Scheme I).

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**References**