

## The Nuclear Alkylation of Arylamines by Trialkyl Phosphates

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TRIALKYL PHOSPHATES can function as alkylating agents and their employment in the *O*-alkylation of phenols<sup>1</sup> and alcohols,<sup>2</sup> the *S*-alkylation of mercaptans,<sup>3</sup> and the *N*-alkylation of thiourea<sup>4</sup> and arylamines<sup>5</sup> has been recorded. We have now found that trialkyl phosphates may also be used in the preparation of nuclear-methylated aromatic compounds. Thus, one mole of 2-naphthylamine reacts with two moles of trimethyl phosphate at 250—275° for 2 hr. to yield 1-methyl-2-dimethylaminonaphthalene (64%) and 2-dimethylaminonaphthalene (10%).

A decrease in the molar proportions of triester to amine to 1:1 reduces the yield of nuclear-methylated product to less than 10%. An increase to 4:1 produces approximately the same result but this latter effect may be attributable to depression of the reaction temperature by the excess of triester (b.p. 193°). Reactions carried out below 220° have been found to yield 2-dimethylaminonaphthalene exclusively. Nuclear methylation takes place with increasing ease along the series: 1-naphthylamine < 2-naphthylamine < 4-methyl-2-naphthylamine.

The latter two arylamines gave only 1-methyl

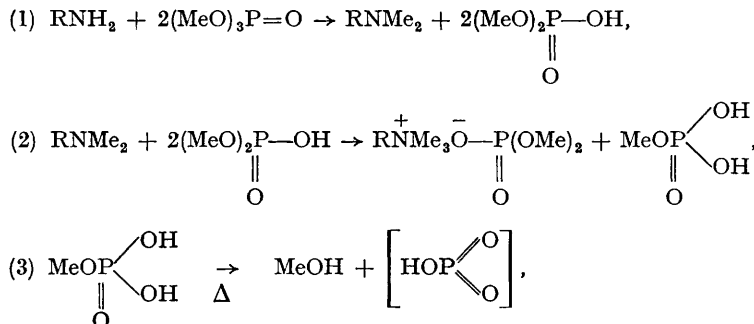
derivatives whereas the products from 1-naphthylamine were monomethylated in the 2- and 4-positions. A little 2,4-dimethylated compound was also formed on prolonged heating. Aniline, 2,4-xylidine, and 2,6-xylidine yielded only *N*-methylated derivatives although 3,5-xylidine gave small quantities of products methylated in the nucleus in the 2- and 4-positions.

Reaction between 2-naphthylamine and triethyl phosphate has been found to give small yields of nuclear-ethylated product.

There is evidence that the nuclear methylation reaction between trimethyl phosphate and 2-naphthylamine may proceed by the formation and subsequent thermal decomposition of the quaternary salt 2-naphthyltrimethylammonium dimethyl phosphate. Paper-chromatographic studies indicate that this material is present in quantity during the early stages of reaction. The addition of sodium iodide to an aqueous solution of the reaction mixture taken at this stage precipitates 2-naphthyltrimethylammonium iodide in 50% yield. Moreover the quaternary iodide reacts with trimethyl phosphate in hot ethyl methyl ketone to yield the above quaternary dimethyl phosphate

and this product on heating at 250° gives 1-methyl-2-dimethylaminonaphthalene with some 2-dimethylaminonaphthalene.

The formation of 2-naphthyltrimethylammonium dimethyl phosphate may take place by the following overall steps:



where R = 2-naphthyl.

Evidence for step (2) is provided by heating 2-dimethylaminonaphthalene with dimethylphosphoric acid. A water-soluble gum with the paper-chromatographic characteristics of the quaternary salt is first formed. More prolonged heating at 250° yields 1-methyl-2-dimethylaminonaphthalene.

Salts of dimethylphosphoric acid are reported to undergo thermal decomposition near 250°<sup>6</sup> and the isolation of trimethyl phosphate<sup>7</sup> suggests

an initial disproportionation although any mono-methyl phosphates produced in this way seem unlikely to survive at this temperature. Rearrangement of the quaternary cation may thus accompany decomposition of the diester anion. In the case of the 2-naphthyltrimethylammonium

ion the transfer of a methyl group to the nucleophilic 1-position may be visualised. The concomitant formation of 2-dimethylaminonaphthalene suggests that the transfer of a methyl group to another species such as the dimethylphosphate anion or one of its products of decomposition may also be taking place. Where a less active aromatic position is available, as in aniline, reaction may proceed solely by this route.

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