Reaction of Phenacyltriphenylarsonium Bromides with *N*-Methylaniline and *N*,*N*-Dimethylaniline

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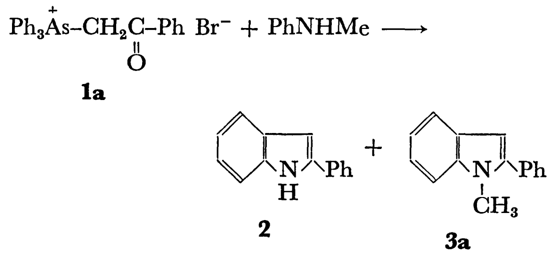
Synopsis. Reaction of phenacyltriphenylarsonium bromide with *N*-methylaniline furnished 2-phenylindole predominantly together with 1-methyl-2-phenylindole. The corresponding reaction of the arsonium salt with *N*,*N*-dimethylaniline did not give any indole, instead a simple nucleophilic substituted product, α-4′-(dimethylamino)deoxybenzoin was obtained. But, the latter reaction on being carried out in presence of hydrobromic acid afforded 1-methyl-2-phenylindole by the demethylation of *N*,*N*-dimethylaniline.

In an earlier communication,[1] we reported the reaction of phenacyltriphenylarsonium bromide with anilines leading to the formation of 2-arylindoles and it was shown that the nucleophilic addition of aniline to the carbonyl group of the arsonium salt preceded the formation of the ylide. In an attempt to extend this reaction to aromatic secondary and tertiary amines, we carried out the reactions of phenacyltriphenylarsonium bromide(s) with *N*-methylaniline and *N*,*N*-dimethylaniline. The results obtained were quite interesting and could be explained on the basis of the mechanism we proposed earlier.[1]

Results and Discussion

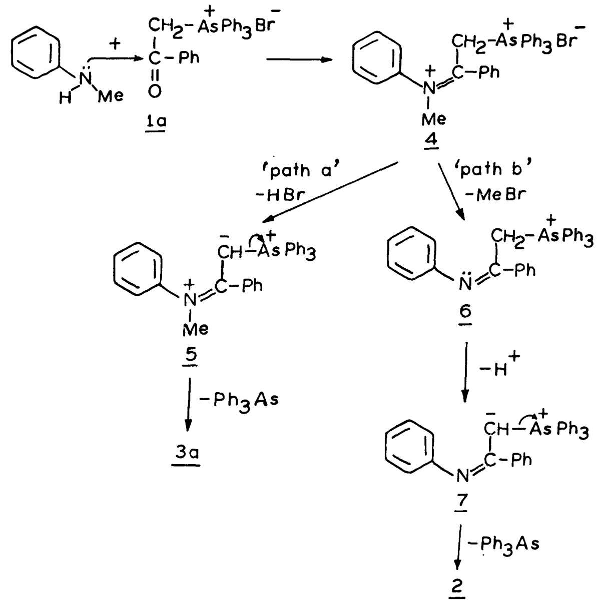
Phenacyltriphenylarsonium bromide (**1a**) reacted with *N*-methylaniline to give 2-phenylindole (**2**, 50%) and 1-methyl-2-phenylindole (**3a**, 5%). *N*-Methylaniline, like aniline, acting as a typical nucleophile interacts with the arsonium salt to form the alkylideneammonium species, **4** (Scheme 1). The formation of **2** indicates that **4** does not follow exactly the same route as observed in the case of aniline[1] because in that event 1-methyl-2-phenylindole would have been obtained exclusively. It appears that the species **4** follows two routes: (i) deprotonation of **4** gives the ylide **5** which subsequently undergoes cyclization *etc.* as observed in the case of aniline,[1] to afford **3a** (path a) and (ii) demethylation of **4** precedes the formation of the ylide **7**, the latter finally gives **2** by cyclization *etc.* (path b). The excess formation of **2** in comparison to **3a** indicates that demethylation of species **4** (path b) is preferred over its deprotonation (path a). An alternative possibility of the initial formation of **3a** followed by its demethylation to **2** is ruled out on the basis of the observations made by Chambers and Pearson[2] in connection with the dealkylation of cyclic amines.



$$\mathrm{Ph_3\overset{+}{A}s\text{-}CH_2\underset{\underset{O}{\|}}{C}\text{-}Ph\ Br^- + PhNHMe \longrightarrow}$$

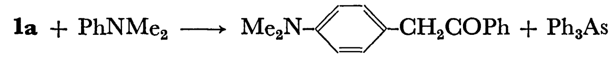
1a

2 **3a**



Scheme 1.

N,*N*-Dimethylaniline behaved in a different manner; it reacted with **1a** to afford simple nucleophilic substitution product, α-4′-(dimethylamino)deoxybenzoin (**8**) and no indole was obtained. This is in accordance with the general behaviour of $PhNMe_2$ towards nucleophilic displacement.[3] When $PhNMe_2$ was refluxed with **1a** in presence of hydrobromic acid, **3a** was obtained in 36% yield. Similarly $PhNMe_2$ reacted with **1b—d** in the presence of HBr to give the corresponding 1-methyl-2-arylindoles (**3b—d**) (Table 1). The results obtained



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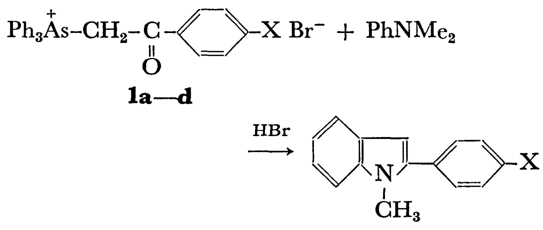

1a—d

3a—d

TABLE 1. 1-METHYL-2-ARYLINDOLES

Compound	X	Yield %	Mp/°C	Lit[4], Mp/°C
3a	H	36	100	99—100
3b	Cl	41	119	118—120
3c	Br	39	115	114—116
3d	OCH_3	35	117—118	118—119

with $PhNMe_2$ can be explained like this. The presence of two bulky methyl groups on nitrogen prevents the donation of its electron pair to the carbonyl group of the arsonium salt. But, in the presence of HBr, *N*,*N*-dimethylanilinium bromide is formed which undergoes facile demethylation to *N*-methylaniline.[2] The latter subsequently reacts with the arsonium salt as described earlier. Further, in the presence of HBr, path b is blocked due to the formation of MeBr from demethylation of $PhNMe_2$ and therefore only **3a** is formed.

$$PhNMe_2 + HBr \longrightarrow Ph\overset{+}{N}HMe_2Br^- \rightleftharpoons PhNHMe + MeBr$$

Experimental

General Procedure. Arsonium salt (10 mmol) and PhNHMe or $PhNMe_2$ (20 ml) were refluxed for 7 h. The reaction mixture was taken in chloroform, washed with 10% aqueous hydrochloric acid solution and then with water. The chloroform extract was chromatographed on silica gel. Elution with pet. ether (60—80 °C) and pet. ether–benzene (1:1) furnished Ph_3As (mp 60 °C) and the corresponding indole(s) respectively. Reaction of the arsonium salt with $PhNMe_2$ in the presence of HBr (4 ml) was carried out in a similar manner.

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References

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