Tetrahedron Letters No. 22, pp 1923 - 1926, 1977. Pergamon Press. Printed in Great Britain.

REACTION OF PHENACYLTRIPHENYLARSONIUM BROMIDE WITH ANILINES: SYNTHESIS OF 2-PHENYLINDOLES THROUGH ARSENIC YLIDE

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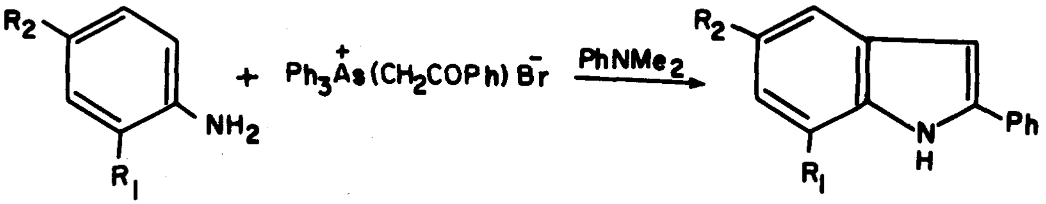
(Received in UK 29 March 1977; accepted for publication 15 April 1977)

The phenacyltriphenylarsonium bromide on refluxing with anilines in N,N-dimethylaniline furnishes the corresponding 2-phenylindoles. The experimental results lead to the conclusion that in the reaction, nucleophilic addition of aniline to the carbonyl group of the arsonium salt precedes the ylide formation.

The arsonium ylides have been used for the synthesis of olefins[1], cyclopropanes[2,3], aziridines[3], 5-hydroxyisoxazolines[4] and a number of other heterocyclics[5]. We now report the synthesis of 2-phenylindoles(3a - f)from the reaction of phenacyltriphenylarsonium bromide(2) with the anilines (1a - f).



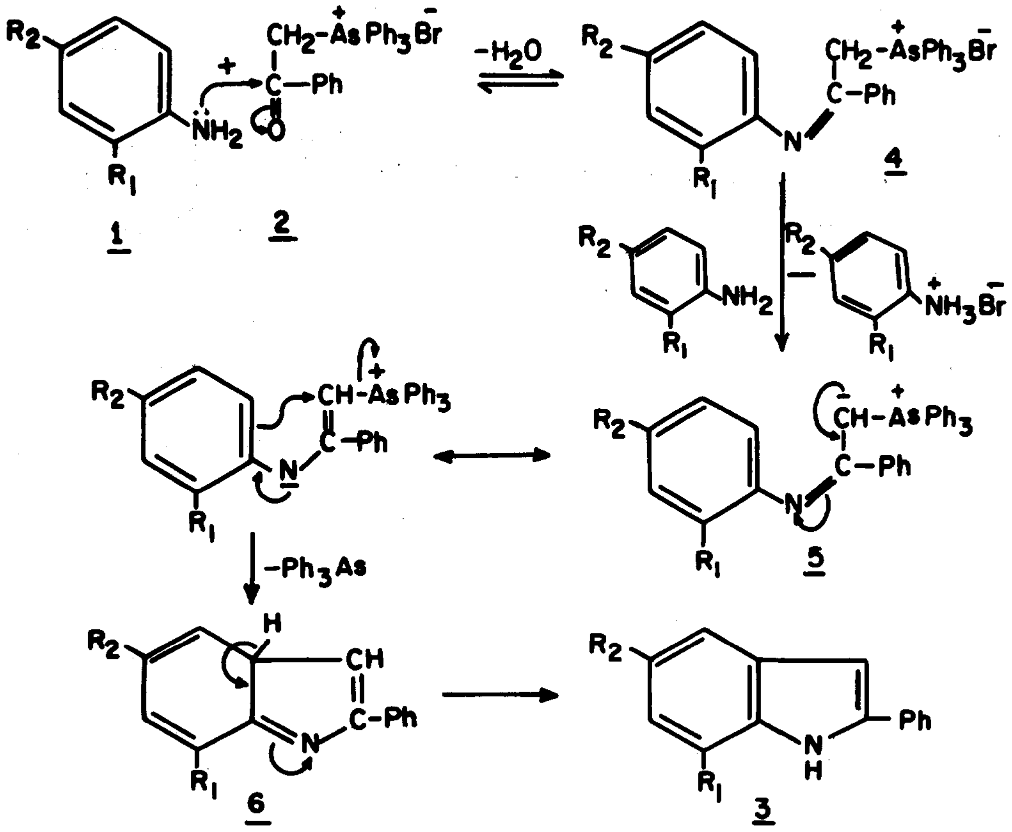
1a-f 2 3a-f

The aniline 1(30 mmol), phenacyltriphenylarsonium bromide 2 (10 mmol) and N,N-dimethylaniline (40 ml) were refluxed for four hours. The reaction mixture was, thereafter, neutralized with 20% aqueous HCl and extracted with ether. The ether extract after washing with water was finally dried and the residue on crystallization from an appropriate solvent furnished the corresponding 2-phenylindole. The motherliquor on further work-up afforded triphenylarsine (m.p. 60°). In this connection, it was found that an excess of aniline was essential for a satisfactory yield, because the use of 20 mmol aniline afforded only 9.01 per cent yield of the indole. All the indoles (Table 1) were fully characterized by colour reaction[6], IR and ^{1}H NMR spectra.

TABLE 1

Product	R_1	R_2	m.p.	Lit. m.p.	Yield %
3a	H	H	187°	186-188°[7]	58
3b	CH_3	H	117°	118°[8]	63
3c	H	CH_3	132°	134°[8]	53
3d	H	Cl	192-194°	195°[8]	51
3e	NO_2	H	80°	-	70
3f	H	NO_2	198°	201°[9]	72

A plausible mechanism of the reaction of phenacyltriphenylarsonium bromide with aniline has been shown in scheme 1 .



SCHEME 1

Another possible route for the formation of species 5, could be via initial conversion of the arsonium bromide into the ylide, $Ph_3\overset{+}{As}\overset{-}{C}HCOPh$, followed by its further reaction with aniline. This possibility is, however, discarded in view of the fact that the enhanced stability of the ylide resulting from delocalization of the negative charge onto carbonyl oxygen is expected to greatly diminish its reactivity towards aniline. This is further supported by the results of an another synthesis of 2-phenylindole (3a) using $Ph_3\overset{+}{As}\overset{-}{C}HCOPh$, obtained by the method of Johnson et al.[10] (m.p. 172°, ν_{CO} 1570 cm^{-1}). In this experiment, anilinium bromide (10 mmol), phenacylidenetriphenylarsorane (10 mmol) and aniline (20 mmol) were refluxed in N,N-dimethylaniline and the resulting reaction mixture was worked up in the manner described above. The yield of 2-phenylindole was comparable with that obtained in the first method. It was, however, found that the presence of anilinium bromide was essential in this method, as in its absence no 2-phenylindole could be obtained. The ylide, $Ph_3\overset{+}{As}\overset{-}{C}HCOPh$ being a stronger base than aniline, would react with anilinium bromide to form aniline and phenacyltriphenylarsonium bromide, the latter subsequently reacting with aniline as shown in scheme 1.

This method of the synthesis of 2-phenylindoles has the apparent advantage over the other two methods[8,11] as in this case the starting material, triphenylarsine, can be recovered easily.

Acknowledgements : We are indebted to Prof. R.C. Mehrotra without whose generous encouragement this work would have not been possible. Thanks are also due to Prof. K.C. Joshi for helpful suggestions. One of us (S.K.S.) acknowledges the financial assistance from U.G.C., New Delhi.

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