ARYLATION OF ANIONS BY DIPHENYLIODONIUM FLUOBORATE IN TWO-PHASE SYSTEMS

V. V. Grushin, T. P. Tolstaya,
and I. N. Lisichkina

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The arylation of nucleophiles using diaryliodonium salts has been well studied and is widely used in organic synthesis [1]. We found that running such reactions in two-phase systems (H_2O/CH_2Cl_2 or $H_2O/CHCl_3$) leads to a sharp increase in the reaction rate when compared with reaction in water, aqueous alcohols [2], or dioxane [3], and in some cases also to an increase in the yield of the desired product. The experimental results are given in Table 1.

It should be mentioned that the reactions studied by us proceed under the same conditions and at the same rate both in the presence and absence of the Makosza catalyst. This interesting fact is apparently explained by the fact that the diphenyliodonium cation under these conditions simultaneously functions both as the substrate and as the lipophilic cation — the transfer agent of the unsolvated anion in the organic phase.

Judging by the $PhI/PhNO_2$ ratio (see Table 1), which within the limits of experimental error does not change with change in the conditions, the mechanism of the reaction in two-phase systems is the same as in water [2].

EXPERIMENTAL

Reaction of $Ph_2I^+BF_4^-$ with $NaNO_2$ in $H_2O/CHCl_3$ System. A mixture of 1 g of $Ph_2I^+BF_4^-$(I), 2 g of $NaNO_2$, 5 ml of H_2O, and 10 ml of $CHCl_3$ was vigorously stirred at 40-50°C until all of the iodonium salt had decomposed (2.5 h). The organic layer was studied by the GLC method. The $PhI/PhNO_2$ ratio was found to be 1.05:1.

Under the same conditions the same mixture in the presence of 0.15 g of $[PhCH_2\overset{+}{N}Et_3]Br^-$ gave a $PhI/PhNO_2$ ratio equal to 1.02:1.

TABLE 1

Solvent	Time, h	T., °C	$PhI/PhNO_2$ mole ratio*	Yield of phenyl p-tolyl sulfone, %	Recovered starting salt, %
$Ph_2I^+BF_4^-+NaNO_2 \rightarrow PhNO_2+PhI+NaBF_4$					
$H_2O/CHCl_3$	2,5	40–50	1,05 : 1	–	0
$H_2O/CHCl_3$ in presence of $[PhCH_2N^+Et_3]Br^-$	2,5	40–50	1,02 : 1	–	0
H_2O	2,5	40–50	1,07 : 1	–	86
$CHCl_3$	2,5	40–50	–	–	96
$PhI^+BF_4^-+p\text{-}MeC_6H_4SO_2Na \rightarrow p\text{-}MeC_6H_4SO_2Ph+PhI+NaBF_4$					
$H_2O/CHCl_3$	1	50	–	94	0
80% aqueous alcohol†	4	78	–	56 ‡	39

*Based on the GLC data.

†From [2].

‡Based on unreacted $Ph_2I^+Br^-$.

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Reaction of $Ph_2I^+BF_4^-$ with $NaNO_2$ in Water. A solution of 1 g of (I) and 2 g of $NaNO_2$ in 6 ml of water was stirred at 40-50° for 2.5 h, after which it was diluted with water up to 40 ml, the nonsalt reaction products were extracted with ether, and the aqueous layer was treated with NaI to precipitate the $Ph_2I^+I^-$, which was washed well with water and dried in vacuo over P_2O_5. Its yield was 0.95 g (86% when based on starting (I)), mp 182° (decompn.) (cf. [4]).

The $PhI/PhNO_2$ ratio in the ether extracts, determined by GLC, was equal to 1.07:1.

Reaction of $Ph_2I^+BF_4^-$ with $NaNO_2$ in $CHCl_3$. A suspension of 0.5 g of (I) and 1 g of $NaNO_2$ in 5 ml of dry $CHCl_3$ was stirred vigorously for 2.5 h at 40-50°, after which it was extracted well with water, and treatment of the water extracts with NaI gave a precipitate of 0.53 g [96% when based on taken (I)] of $Ph_2I^+I^-$.

Reaction of $Ph_2I^+BF_4^-$ with $p\text{-}MeC_6H_4SO_2Na$ in $H_2O/CHCl_3$ System. A mixture of 1 g of (I), 1.6 g of sodium p-toluenesulfinate, 6 ml of H_2O, and 11 ml of $CHCl_3$ was vigorously stirred at 50° until all of the iodonium salt had decomposed (1 h). The organic layer was evaporated, and an ether solution of the residue was passed through an Al_2O_3 column. The ether was evaporated, and the addition of hexane to the residue gave 0.59 g (94%) of phenyl p-tolyl sulfone with mp 126.5-127.5° (cf. [2]).

CONCLUSIONS

The rate of phenylating nitrite and p-toluenesulfinate anions by diphenyliodonium fluoborate increases sharply in two-phase systems.

Here the diphenyliodonium fluoborate functions as an interphase catalyst.

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