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DIAZO TRANSFER REACTION MEDIATED BY PHASE-TRANSFER CATALYSTS

M. Nakajima and J.-P. Anselme*

Department of Chemistry
University of Massachusetts at Boston, Boston, MA 02125

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The *diazo transfer* reaction to amine anions has been shown to be a useful azide synthesis.[1] The need to utilize[2] strong bases such as alkyllithium reagents to generate the amine anions prompted us to investigate phase-transfer catalysis.[2] Treatment of aniline with tosyl azide in benzene-sodium hydroxide with stirring in the presence of benzyltriethylammonium (BTEA) chloride gave phenyl azide, isolated as its triphenylphosphine imine adduct in 46% yield. The yields of aryl azides seem to parallel the "acidity" of the amine (see Table I).

$$\underset{(387\ \text{mmoles})}{PhNH_2} + \underset{(25\ \text{mmoles})}{TosN_3} \xrightarrow[\Delta,\ \text{BTEA Cl}^-]{50\%\ \text{NaOH, benzene}} PhN_3\ (\text{as its } Ph_3P \text{ adduct})$$

The yield of phenyl azide rose from 35% to 94% when the ratio of amine to tosyl azide was increased from 10 to 50.

The nature of the catalyst apparently plays a role in the *diazo transfer* reaction in agreement with Dockx' results.[2a]

Table 1. Aryl Azides *via* Diazo Transfer with Tosyl Azide[a]

	$ArNH_2$		$TosN_3$		$ArN{=}PPh_3$ (mp)
	Ar	mmoles	(mmoles)	(% yield)	(% yield)
1)	Ph	500	10	—	94 (131-132°)
2)	Ph	387	25	—	46 (131-132°)
3)	Ph	100	10	—	35 (131-132°)
4)	*p*-BrPh	100	10	68	62 (122-124°)
5)	*p*-ClPh	100	10	46	59 (115-116°)
6)	*p*-CH_3Ph	100	10	18	8 (134-135°)

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a) All reactions were carried out at reflux in benzene (50 ml) using 30 ml of 50% sodium hydroxide and BTEA chloride as catalyst for 48 hrs. The yields of azides are based on tosyl azide.

With aliphatic amines, the yields were lower. Benzyl azide was isolated in 28% yield (average of two runs) while dibenzylamine gave benzaldehyde in 38% yield in addition to trace amounts of benzal dibenzylhydrazine and an unknown product. Benzaldehyde would be the expected product of the base-catalyzed elimination of hydrazoic acid from N-azido dibenzylamine[3]

Table 2. Phenyl Azide via Diazo Transfer with Tosyl Azide with Various Phase-Transfer Catalysts[a]

	Catalyst	Yield of PhN_3 (as $Ph_3P{=}NPh$)
1)	$(\underline{n}\text{-}C_6H_{13})_4N^+Br^-$	40%
2)	$PhCH_2N^+(C_2H_5)_3Cl^-$	35%
3)	$(CH_3)_4N^+Cl^-$	31%
4)	$(\underline{n}\text{-}C_4H_9)_4N^+Br^-$	21%
5)	$\underline{n}\text{-}C_3H_9N^+(\underline{n}\text{-}C_8H_{17})_3Br^-$	19%

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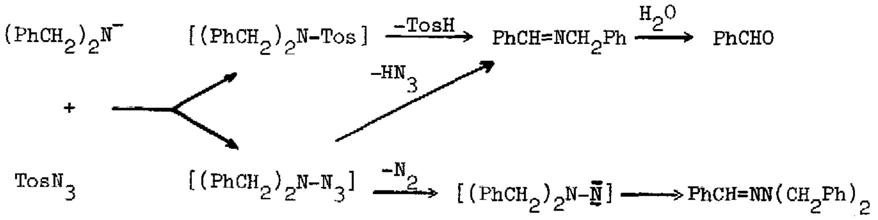
a) All reactions were carried out as described in Table 1, using 100 mmoles of aniline, 10 mmoles of tosyl azide 0.1 mmole of catalyst.

or more likely of p-toluenesulfinic acid from N-tosyl dibenzylamine, while the formation of the hydrazone must be viewed as arising via diazene-hydrazone rearrangement of the N-nitrene.[3]



Evidently, in this case an azido transfer reaction[4] occurred to produce the N-azide, at least to a small extent. Cyclohexyl azide was obtained in 51% yield from the reaction of a 50-fold excess of cyclohexylamine and tosyl azide.

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