

## On the Conversion of Azides to Diazo Compounds

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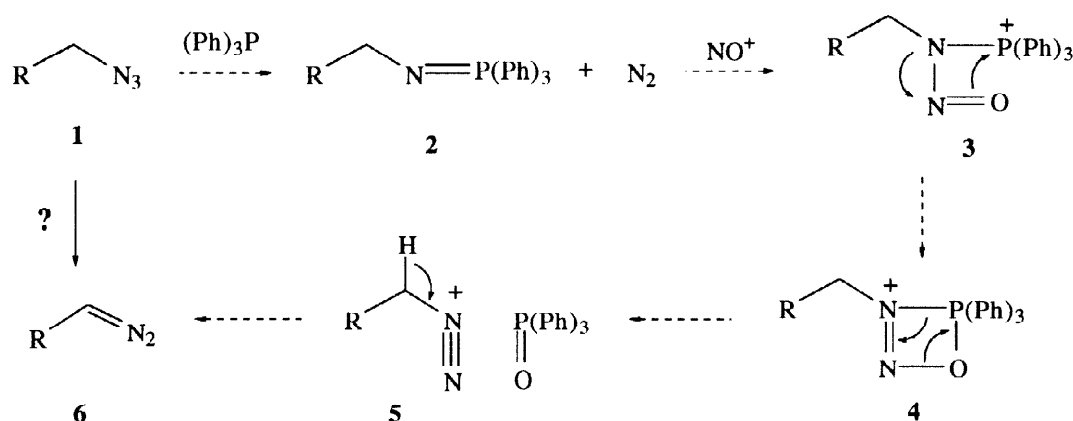
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**Abstract:** The ability to convert a suitably disposed azide group into the corresponding diazo compound has been demonstrated. © 1998 Elsevier Science Ltd. All rights reserved.

A variety of chemically distinct procedures have been developed for installation of the diazo functional group into organic molecules. Methods range from exceedingly mild diazo transfer reactions to the harsher, more traditional, diazotization of amines.<sup>1</sup>

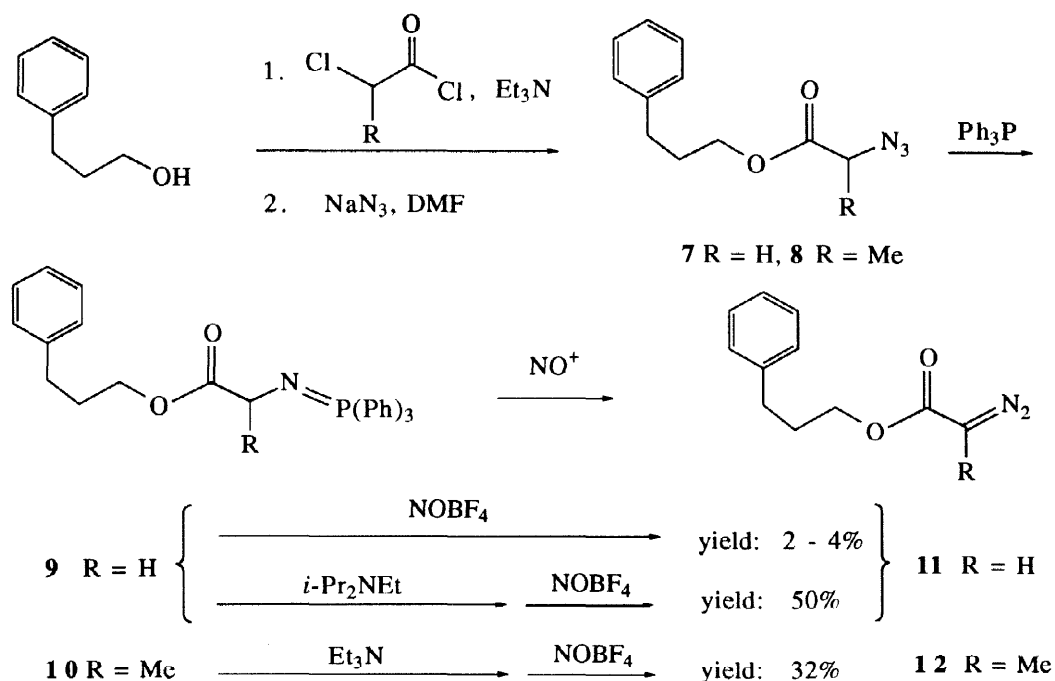
From a purely visual standpoint, the three contiguous nitrogens of an azide group make it alluring as a possible starting material for the preparation of diazo compounds. Surprisingly, studies dealing with the conversion of azide moieties into diazo groups (**1** → **6**) have not been reported. Preliminary studies concerning this possibility are presented below.

A plan was devised based on the sequence of events that might occur upon nitrosation of readily available iminophosphoranes **2**. Formation of the diazo product was anticipated to arise from mechanistic steps reminiscent of the Wittig reaction (**Scheme I**).



If the proposed mechanistic scheme is viable, highly reactive diazonium intermediate **5** would benefit from a predisposition for proton elimination (e.g. R = an electron withdrawing group); this would facilitate formation of the desired, more stable, diazo compound **6**. A simple model system, **7**, was constructed to evaluate this idea (**Scheme II**).

Treatment of azide **7** under Staudinger conditions<sup>2</sup> (triphenylphosphine, CH<sub>2</sub>Cl<sub>2</sub>, RT, 1 Hr.) was accompanied by steady nitrogen evolution to afford iminophosphorane **9**. The mixture was cooled to -78°C and nitrosonium tetrafluoroborate (NOBF<sub>4</sub>) was added in a single portion. After warming to RT and stirring for several hours, a single yellow band was observed by thin layer chromatography. After isolation and spectroscopic analysis, this product was determined to be the anticipated diazo compound **11**.<sup>3</sup> Only a trace quantity of this material was obtained: estimated yield 2 - 4%. The balance of the product mixture consisted of extremely polar, decomposition material.



Scheme II

Despite the nominal yield, isolation of the anticipated diazo product was encouraging. Decomposition was attributed to sluggish deprotonation of intermediate **5** *en route* to diazo compound **6** (**11**). If proton abstraction was the culprit, it seemed logical to attempt to accelerate this step by adding base to the reaction mixture. Indeed, treating the phosphorimine **9** with Hunigs base prior to addition of the nitrosating agent **increased the yield more than 10 fold!**

In a similar fashion, albeit in lower yield, the analogous secondary azide **8** was transformed into corresponding diazo compound **12**.<sup>4</sup>

This study shows that suitably disposed azide groups can be transformed into the diazo functionality *via* the corresponding iminophosphoranes. While the impact of base on product formation clearly has mechanistic implications, no other information is presently available to substantiate the proposed reaction mechanism.

**Acknowledgment** Special thanks to Ms. Kim Carvajal and Marie Casimir for the preparation of key intermediates.

### References and Notes

- For an excellent review see: Regitz, M.; Maas, G.; *Diazo Compounds - Properties and Synthesis*; Academic Press: Orlando, 1986; Part II.
- (a) Golobolov, Y. G., Zhmurova, I. N., Kasukhin, L. F. *Tetrahedron* **1981**, *102*, 437 (b) Staudinger, H., Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635.
- <sup>1</sup>H NMR 300MHz (CDCl<sub>3</sub>) δ 7.3-7.17 (m, 5H), 4.74 (s 1H), 4.18 (t, 2H), 2.66 (t, 2H), 1.98 (quin., 2H): IR (cm<sup>-1</sup>) 2109, 1693: MS (M+1) 205.1 (Agrees with published data: *J. Org. Chem.* **1996**, *61*, 9146.)
- <sup>1</sup>H NMR 300MHz (CDCl<sub>3</sub>) δ 7.31-7.17 (m, 5H), 4.17 (t, 2H), 2.69 (t, 2H), 2.08-1.93 (m, 2H), 1.96 (s, 3H): IR (cm<sup>-1</sup>) 2081, 1691: MS (M+1) 218.9