

SYNTHESIS OF TERTIARY ALKYL AZIDES

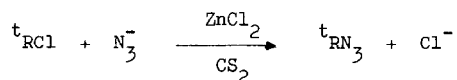
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Alkyl azides are extremely useful intermediates for the synthesis of amines, and nitrogen heterocycles and their preparation and reactions have attracted much attention in recent years.¹ Although primary and secondary azides are conveniently prepared by alkylation of azide ion,^{1b} the preparation of tertiary azides usually involves generation of hydrogen azide and its in situ addition to olefins,² or reaction with tertiary alcohols³. The acidic conditions of these reactions can be avoided by the use of mercuric azide⁴, but this route is restricted to terminal alkenes or strained cyclic alkenes. A few cases of displacement of tertiary halides by azide have been reported^{5,3b}, but these require prolonged reaction times, often at elevated temperatures, and generally⁶ give poor yields.

There is therefore a need for a mild, general, and efficient route to tertiary azides, and this report is concerned with the development of a tertiary azide synthesis (see equation which offers all these features. The synthesis is based on the use of inorganic salts to catalyse organic functional group exchange, as has already been reported⁷ for the preparation of hindered alkyl iodides, using ferric chloride as catalyst.



In the present work, zinc chloride (reagent grade, anhydrous powder) is used as the catalyst, and the exchange is achieved by stirring, at room temperature in carbon disulphide, a mixture of a tertiary chloride (1 mole), sodium azide (2 mole) and zinc chloride (0.2 - 0.4 mole). The exchange is quite slow (10 h to 100 h) but is very clean, and the only other reaction observed under these conditions is β -elimination, but this has either not been detected, or has never accounted for more than 5% of the product. With acyclic

azides, the yields are high (Bu^tN_3 , 96%; Am^tN_3 , 89%) and compare favourably with recent work using DMF^{3b} or MeOH^{5a} as solvent. Cyclic tertiary chlorides are also exchanged, although these exchanges usually require longer reaction times to go to completion. The yields are, however, still good (1-methylcyclohexyl azide, 86%; 1-adamantyl azide, 72%) and again compare well with other exchange procedures^{5b,c}.

The conditions of these reactions (inert solvent, heterogeneous mixture), and the structural requirements for exchange (tertiary, allylic or benzylic azides only), suggest that the exchange proceeds by generation, and in situ trapping, of an ion-pair with carbenium character. Further work is in hand to establish the mechanism more firmly, and to exploit the synthetic potential of these reactions.

References

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