A New Synthesis of Triazane Derivatives

By D. J. BLACKSTOCK and D. A. R. HAPPER*

(*Department of Chemistry, University of Canterbury, Christchurch, New Zealand*)

UNLESS stabilised by unsaturation, chains of more than two nitrogen atoms are easily broken. Of the open-chain compounds consisting of three linked nitrogen atoms, both azides and triazenes are well known and moderately stable. The triazanes, however, are much rarer;[1] we now report a new reaction leading to the formation of triazane derivatives, which although of limited applicability, has several novel features.

Acetone 2-phenylsemicarbazone reacts quantitatively with one mole of iodine.[2] When investigated, the reaction was found to be a Hofmann rearrangement, the initial product of the reaction being the isocyanate (I).

$$\mathrm{Me_2C{=}N{\cdot}NPh{\cdot}CO{\cdot}NH_2} \xrightarrow{I_2} \underset{\text{(I)}}{\mathrm{Me_2C{=}N{\cdot}NPh{\cdot}N{=}C{=}O}} + \mathrm{2HI}$$

Most remarkable is the stability of the isocyanate (I). The only other case of an isocyanate group linked directly to nitrogen is that of dimethylamino-isocyanate, recently reported[3] to exist as a dimer with a rather novel nitrogen ylid structure. The isocyanate (I), on the other hand, is sufficiently stable for it to be extracted from aqueous alcohol or aqueous acetone solution. Furthermore, it is easily purified by distillation under reduced pressure (b.p. 91—93°/0·5 mm.) and passes through a gas chromatograph without significant decomposition. The proposed structure for (I) is supported by elemental analysis, n.m.r. and i.r. spectrometry (v. strong peak at 2230 cm.$^{-1}$). Although (I) is moderately stable in aqueous solution, it reacts smoothly with alcohols and amines to give ureas or urethanes that are triazane derivatives.

$$\mathrm{Me_2C{=}N{\cdot}NPh{\cdot}N{=}C{=}O} \xrightarrow{\mathrm{H{-}Y}} \mathrm{Me_2C{=}N{\cdot}NPh{\cdot}NH{\cdot}CO{\cdot}Y}$$

$$-\mathrm{Y} = -\mathrm{OMe},\ -\mathrm{OEt},\ -\mathrm{OBu^t},\ -\mathrm{NH_2},\ -\mathrm{NC_5H_{10}}$$

Alternatively, the triazanes may be prepared directly from the semicarbazone by reaction with iodine (1 mole) and the sodium alkoxide (3 moles) using the alcohol as solvent. By this means overall yields of 80—85% can be obtained. This direct method was unsuccessful for the formation of t-butylurethane, giving only a black tar. However, the derivative could be prepared quite readily from the isocyanate by reaction with a solution of potassium t-butoxide in t-butanol. The urea derivatives could be prepared either indirectly, from the isocyanate, or directly from the semicarbazone by replacing one of the three moles of alkoxide by the desired amine or ammonia.

Acetone 2-phenylthiosemicarbazone also reacted with iodine under exactly the same conditions as the semicarbazone to give an isothiocyanate in 65% yield. From this compound a series of thiourethanes could be prepared, but reaction was very much slower in this case, and heating under reflux in alkoxide–alcohol solutions was necessary before reaction would occur at a reasonable rate.

The triazane derivatives proved to be stable low-melting solids, pale yellow in colour. The structures were based on elemental analyses, i.r. and n.m.r. data, and their relationship to the isocyanate (I). Although stable in the solid state they decompose rapidly in solution, even in non-polar solvents such as chloroform or carbon tetrachloride.

The Hofmann rearrangement leading to the formation of the isocyanate and isothiocyanate is unusual for several reasons. Although one or two examples of Hofmann rearrangements of urea derivatives have been reported in the past,[4] the yields have invariably been poor. The yield in this case is very high. The reagent used is also unusual. There appears to be no other example of the use of iodine as the halogen for the rearrangement. Bromine can be used but the yields are lower. Not only is iodine a very effective reagent, but the reaction does not even require the presence of strong alkali; it goes to completion in about 10 min. at 50° in phosphate or acetate buffers (pH 5—7).

Finally, the rearrangement of the thiosemicarbazone to give the isothiocyanate is the only case to date in which a thioamide or thiourea has undergone the Hofmann reaction.

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