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THERMOLYSIS OF CARBAMOYL AZIDES III.[1] THE STRUCTURE OF AROMATIC AMINOISOCYANATE DIMERS AND A NEW TRIMERIC AMINOISOCYANATE.

Marlyse Kurz and Werner Reichen*

Institut de chimie organique, Université de Lausanne, CH-1005 Lausanne, Switzerland

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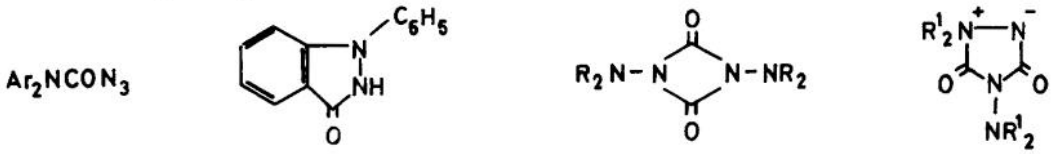
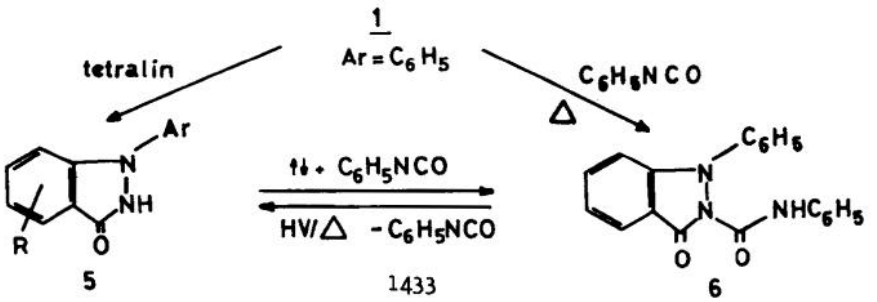
In 1928 Stolle[2] investigated the thermolysis of various diarylcarbamoyl azides 1. Along with the corresponding indazolones 2 as main products, he isolated (in a few cases) small amounts of a dimeric species to which a diazetidine type structure 3 was attributed[3]. Since it is somewhat hard to explain the chemistry of 3 based on the proposed structure and since it is known that dialkylaminoisocyanates dimerize to 5-membered cyclic 1,2-aminimides 4[4] we reinvestigated part of Stolle's work.



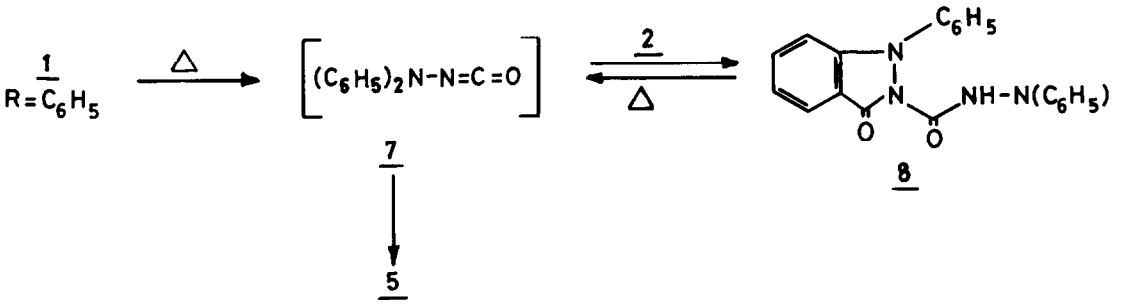
1 2 3 4

When diphenylcarbamoyl azide 1 (Ar=C_6H_5) was thermolyzed in boiling tetralin a 97% yield of the indazolone 5 was isolated along with intractable oily material. When the solvent was replaced by phenylisocyanate a nearly quantitative yield of 2-carbanilino-1-phenylindazolone 6 was obtained. The structure of this compound has been established by independent synthesis. Thus, refluxing 1-phenylindazolone 5 with phenylisocyanate resulted in a complete 1:1 addition to 6 while heating of 6 in high vacuum reformed quantitatively 5 and



5 6

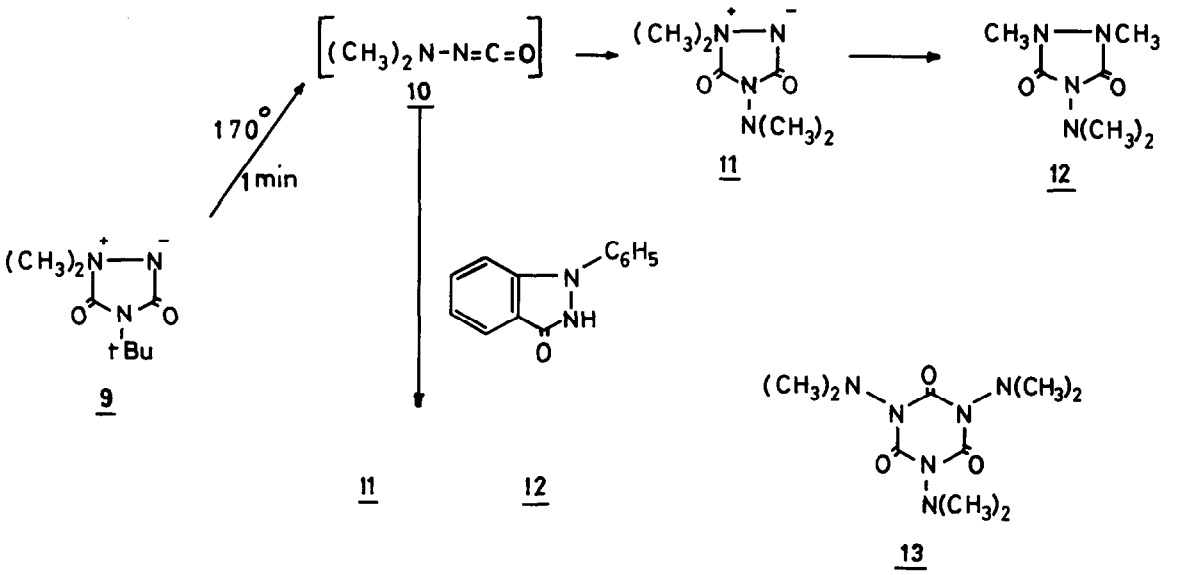
phenylisocyanate. A similar reversible addition has been reported for 1-phenyl-benzimidazolone and p-tolylisocyanate[5]. It is therefore reasonable to assume an indazolone-isocyanate adduct structure 8 for the dimeric diarylaminoisocyanates and at the same time it can be explained easily why yields of these dimers 8 were always low, if any were formed: the intramolecular cyclization of the aminoisocyanate 7 to the indazolone 5 competes effectively with the formation of the dimers. Furthermore, the dimerization is reversible at the temperature needed for the generation of 7 from the starting azide 1. Even when a mixture of 5 and 1 (ratio 5:1) was kept at 170° for 1 minute and worked up by column chromatography only traces of the dimeric product 8 were obtained (showing a parent peak of 420 mass units in its mass spectrum). Sublimation resulted in a quantitative transformation into indazolone 5.



Diphenylaminoisocyanate 7 prepared by thermolysis of 2',2'-diphenyl-imidazole-1-carbohydrazonic acid according to the method of Staab[6] also resulted in a complete intramolecular cyclization to the indazolone 5, while flash vacuum thermolysis of 1 ($Ar=C_6H_5$) yielded a mixture of at least 15 compounds the main product being diphenylamine. No dimeric product could be detected.

1,1-Dimethyl-4-tert.butyl-1,2,4-triazolidindione-1,2-aminimide 9 is known to dissociate into dimethylaminoisocyanate 10 and tert.butylisocyanate at temperatures above 70° [4], the former dimerizing to 11 if no trapping agent is present. When 9 was thermolyzed neat (1 min., 170°) the cyclization to 11 and 1,2-dimethyl-4-dimethylamino-1,2,4-triazolidindione 12 - a rearrangement product of 11 - occured quantitatively as was shown by nmr. spectroscopy. The dry-thermolysis of 9, well mixed with various amounts of 1-phenylindazolone 5 (0.01 - 3.0 equivalents), however, yielded a trimeric dimethylaminoisocyanate (20-60%, m.p.: 179°) along with the dimeric derivatives 11 and 12. Based on spectral data (ir.(KBr) : 1718, 1408, 1005, 747 cm^{-1}; nmr.($CDCl_3$) : δ 2.95 ppm (s); ms. (m/e^+) : 216, 173, 171, 139, 86(bp.)) and correct elemental analysis we propose its structure as 1,3,5-tris(N,N-dimethylamino)-1,3,5-triazintrione

13. (A somewhat related triazintrione was obtained previously in the thermolysis of dimethylcarbamoyl azide[1]).



The exact way of formation of 13 is not yet known beyond conjecture but most likely a phenylindazolone-isocyanate adduct with a structure like 8 is involved as the first step followed by addition of two more molecules of amino-isocyanate to the free NH-function. At this stage cyclization takes place while the indazolone moiety is set free. It is quite possible that dimerization[7] and trimerization[8] of isocyanates (without additional heteroatomic substituent) which, both, are catalyzed by bases proceed in a similar way.

The thermal behaviour of the trimer 13 is currently under investigation.

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