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TWO SYNTHETIC ROUTES TO 1,3,5-TRIARYL-2-PHENYLIMINO-4,6-DIOXOHEXAHYDRO-S-TRIAZINES

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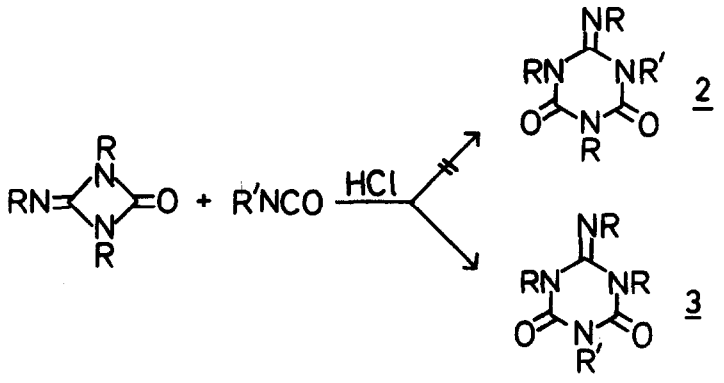
Aryl isocyanates and N,N-diaryl carbodiimides are known to homodimerize and trimerize, yielding 1,3-diazetidines and hexahydro-s-triazine derivatives.(1,2) Both heterocumulenes are also known to react with each other via a [2 + 2] cycloaddition, giving 2-arylimino-1,3-diaryl-diazetidinones.(3) Cycloadducts derived from two moles of aryl isocyanate and one mole of N,N'-diarylcarbodiimide or vice versa have not been synthesized so far.(4,5) We found that 1,3,5-triaryl-2-phenylimino-4,6-dioxo-hexahydro-s-triazines 3 (2:1 cycloadducts from aryl isocyanates and N,N'-diaryl carbodiimide) can be prepared conveniently from 1,3-diphenyl-2-phenylimino-diazetidinone 1 and aryl isocyanates or bis-(chlorocarbonyl) arylamines 4 and N,N',N"-triphenyl guanidine.

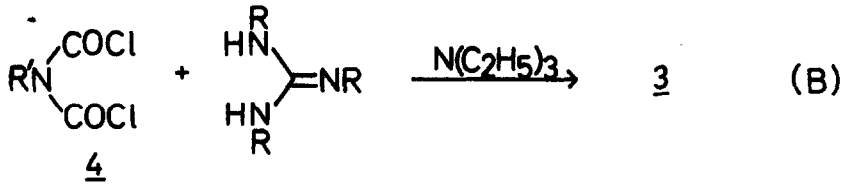
On treatment of a suspension of 1 in excess phenyl isocyanate with gaseous hydrogen chloride at room temperature, 1,3,5-triphenyl-2-phenylimino-4,6-dioxohexahydro-s-triazine 3a is formed in 82% yield. Other aryl isocyanates such as p-tolyl and m-chlorophenyl isocyanate can also be used in the reaction, resulting in the formation of hexahydro-s-triazine derivatives derived from two different aryl isocyanates. Of the two possible structural isomers, 2 and 3, which can be expected from a reaction with a different isocyanate, only 3 is obtained.(6)



(A)

3	R	R′	M.P.	YIELD
a	C_6H_5	C_6H_5	297°	82 %
b	C_6H_5	p-$CH_3C_6H_4$	245-7°	73 %
c	C_6H_5	m-ClC_6H_4	244°	47 %

Proof for the proposed structure of the adducts 3b and c was obtained through independent synthesis of 3b from bis-(chlorocarbonyl)-p-toluidine 4,(7) and N,N',N"-triphenylguanidine in presence of triethylamine (53% yield).

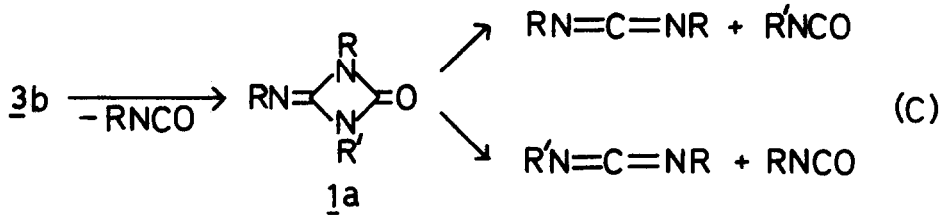


(B)

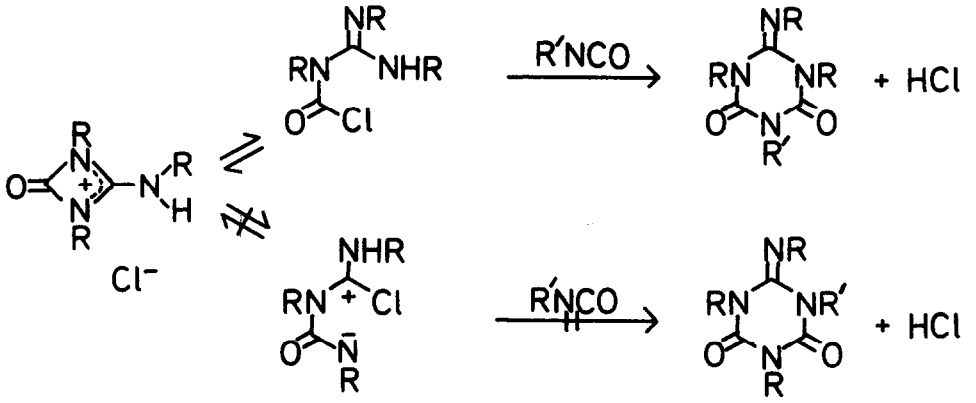
The attempted synthesis of the adduct 3a by treating a mixture of phenyl isocyanate and N,N'-diphenyl carbodiimide(8) with gaseous hydrogen chloride led to the dimerization and trimerization of the carbodiimide, giving varying amounts of 2,4-bisphenylimino-1,3-diphenyl-diazetidine and 1,3,5-triphenyl-2,4,6-tris-phenyl-iminohexahydro-s-triazine. Other, so far unidentified, products are also formed in this reaction.

The ir spectra of the adducts 3a-c (in KBr) show three characteristic bands in the double bond region at about 1750 (weak), 1690 (strong) and 1670 cm^{-1} (strong). The mass spectral fragmentation of 3b and c showed small mass peaks for unsymmetrical carbodiimides R'N=C=NR. This led us originally to believe that the adducts were contaminated by small amounts of the isomeric compounds 2b and c, which can generate R'N=C=NR on thermal decomposition. Since independently

synthesized 3b from reaction (B) shows the same fragmentation pattern, the unsymmetrical carbodiimide has to be formed in a thermal, stepwise decomposition involving the formation of a cyclic 1:1 adduct 1a which dissociates into two different carbodiimide-isocyanate pairs.



The formation of cycloadducts 3 and not 2 in the HCl catalyzed addition of aryl isocyanates to imino-diazetidines 1 can be explained with a specific opening of the four-membered ring in 1, which takes place after initial protonation of the basic imino group. Bond breaking between the positions 2 and 3 in protonated 1 followed by interaction with aryl isocyanate can only lead to 3, while the isomer 2 is formed after bond scission between 1 and 2. A simplified reaction scheme outlining both possibilities is shown below.



1,3,5-Triaryl-2-phenylimino-2,4-dioxohexahydro-s-triazines 3a-c(9)

a) From 2-phenylimino-1,3-diphenyl-azetidinone (1)

A suspension of 3.13 g of 1 in 12.0 g phenyl isocyanate is treated with dry hydrogen chloride (0.8 g) at room temperature until all starting material has dissolved. The yellow reaction mixture is kept at room temperature for 15 hrs., after which the excess phenyl isocyanate is distilled off in vac. The remaining crystalline residue is taken up in acetone, filtered off and washed with acetone and diethyl ether, leaving 3.55 g of 3a (82%), colorless crystals, m.p. 297° (lit.(5) 294-295°).

b) From bis-(chlorocarbonyl)-p-toluidine (4) and N,N',N"-triphenyl guanidine

A solution of 2.32 g of 4 in 25 ml of chloroform is added dropwise over a period of 20 min. to 2.3 g of triethylamine and 2.87 g of N,N',N"-triphenyl guanidine, dissolved in 25 ml of chloroform. The resulting yellow solution is heated under reflux for 40 min., after which the solvent is removed in vac. and the crystalline residue is taken up in 30-40 ml of methanol. The undissolved colorless crystals are filtered off and washed with methanol, leaving 2.4 g of 3b (53%), m.p. 245-247°; the material is identical (ir, mixture m.p.) with a sample of 3b prepared under a).

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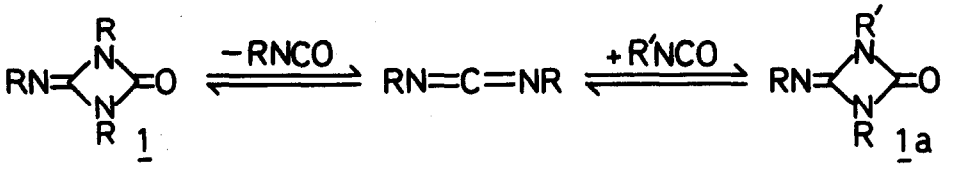
4. Cycloadducts with iminohexahydro-s-triazinedione structure have been prepared from arylsulfonyl isocyanates and N,N'-dialkyl carbodiimide or N-arylsulfonyl-N'-alkyl carbodiimides. H. Ulrich, B. Tucker and A. A. R. Sayigh, J.Amer.Chem.Soc. 90, 528 (1968); H. Ulrich, B. Tucker, F. A. Stuber and A. A. R. Sayigh, J.Org.Chem. 34, 2250 (1969).

5. The isolation of 1,3,5-triphenyl-2-phenylimino-4,6-dioxohexahydro-s-triazine as side product in the phosgenation of carbanilide in hot chlorobenzene was described by D. F. Gavin, W. J. Schnabel, E. Kober and M. A. Robinson, J.Org.Chem. 32, 2511 (1967).

6. Samples of 3b and c are, according to mass spectral data, contaminated by trace amounts of 2:1 adducts containing two moles R'NCO each and one mole RN=C=NR. The formation of these adducts can be explained with a thermal equilibration of the starting material 1 with R'NCO to 1a.



7. G. Zumach and E. Kühle, Synthesis 1970, 542.

8. The uncatalyzed thermal reaction between phenyl isocyanate and N,N'-diphenyl carbodiimide yields only 1; see footnote 3.

9. All compounds gave satisfactory elemental analysis; melting points are not corrected.