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A CONVENIENT THERMAL ROUTE TO N,N-DIALKYLAMINOISOCYANATES

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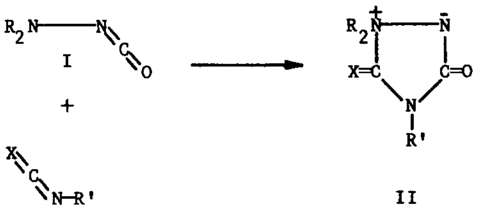
Dialkylaminoisocyanates, I, can be formed as transient intermediates by the photo-Curtius rearrangement of carbamoyl azides, $R_2N\text{-}CO\text{-}N_3$[1], by treating N,N-dialkylaminophosphoramidate anions with CO_2[2], and by the reaction of N,N-dimethyl-N'-dimethylaminoformamidine with aryl isocyanates (resulting in the formation of the aryl isocyanate adducts of I).[3] The aminoisocyanates I add isocyanates (including themselves to form dimers)[2,4] and carbodiimides[4] to form cyclic aminimides II.



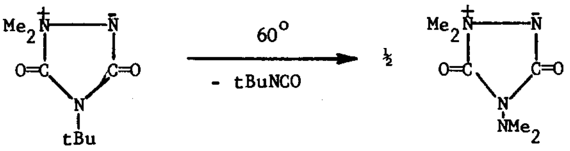
R = alkyl

X = O or R'N

R' = alkyl, aryl, or R_2N

III : R' = tert.-butyl; X = O.

Wishing to extend our studies to addends in whose presence the photolysis of carbamoyl azides is impractical, we sought a thermal reaction producing I under mild conditions and with easily removable by-products. We have found that the formation of cyclic aminimides such as II can generally be reversed thermally, and we have also noted the de-stabilizing effect of bulky groups in the 4-position of II[2]. On this basis, we are now using routinely the 1,1-dialkyl-4-tert.-butyl-1,2,4-triazolidin-3,5-dion-1,2-aminimides III as starting materials for I. Photolysis of the appropriate carbamoyl azides (using 300 nm fluorescent lamps) in the presence of 1.5 to 2 equivalents of tBuNCO gives III in about 40% yield. Commercial tBuNCO has to be purified very carefully by distillation followed by passage through a column (½ x 15") packed with one fifth of the length with neutral alumina (Baker 0540) atop four fifthsof the length of silica gel (Baker 3405), both adsorbents activated at 140°. The tBuNCO is sufficiently pure when the ir spectrum shows virtually no peaks at 3400, 1780, 1760, and 1740 cm^{-1} (0.1 mm path length). The dimethylaminoisocyanate adduct IIIa, 1,1-dimethyl-4-tert.-butyl-1,2,4-triazolidin-3,3-dion-1,2-aminimide[5] melted at 185° (dec) (from chloroform/ether), had C=O absorptions at 1810 and 1710 cm^{-1} ($CHCl_3$), and nmr signals at δ3.19 (s, 6H) and δ1.66 (s, 9H). The mass spectrum shows the parent peak at m/e = 185 and losses of tBuNCO, Me_2N-NCO, MeNCO (presumably via a 1,2 methyl shift), tBu, Me_2N_2 and Me_2N_2H. The corresponding 1,1-diethyl compound IIIb[5], mp 99° (dec) had analogous nmr, ir, and mass spectra. The 4-tert.-butyl adducts III dissociate to their parent isocyanates at temperatures much lower than those required for the corresponding 4-methyl compounds. For example, 1,1-diethyl-4-methyl-1,2,4-triazolidin-3,5-dion-1,2-aminimide (IVb)[4] required heating to 110° in benzyl alcohol to effect dissociation to the isocyanates, trapped by the alcohol to give a 1 : 1 mixture of $PhCH_2OCONHCH_3$ and $PhCH_2OCONHNEt_2$. For the 4-tert.-butyl compound IIIa, heating to 60° sufficed to produce tBuNCO (isolated) and Me_2N-NCO (which dimerized to Va). To obtain addition products from the N,N-dialkylaminoisocyanates, we heat the compounds III in the presence of the desired addend to a temperature at which the new adduct is stable and the dissociation of the III is conveniently rapid, e.g. 95°. Thus, phenyl isocyanate and IIIb were heated to 97° for 30 minutes under a vacuum of 30 mm Hg (to remove tBuNCO). The aminimide VId[5] was isolated in 55% yield, while none of it was obtained when phenyl isocyanate was heated under the same conditions with IVb, which was recovered unchanged.



IIIa Va

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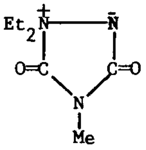
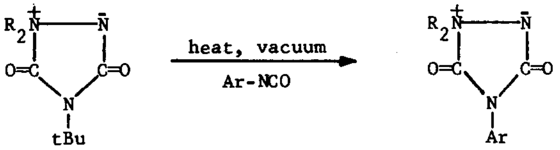


IVb



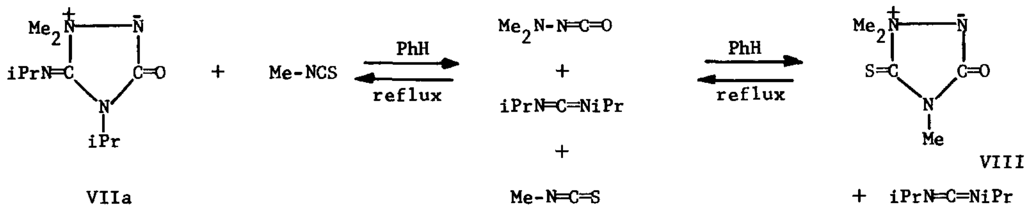
III a : R = Me
b : R = Et

VId, e, f

VId[5] : R = Et; Ar = Ph.
VIe[5] : R = Et; Ar = 1-Naphthyl.
VIf[5] : R = Me; Ar = 1-Naphthyl.

The aminimide VId could also be produced by the photolysis of diethylcarbamoyl azide in the presence of phenyl isocyanate (3.5 equiv.), using p-xylene (33 equiv.) as a singlet photosensitizer to decompose the azide[6]. The yield was only 8%, based on decomposed azide. Triplet photosensitizers did not produce any VId, or any products likely to have arisen from Et_2N-NCO.

The generality of the thermal dissociation of aminimides of the type II is further illustrated by the thermolyses of VII (X = R'N) and VIII (X = S). Photolysis of dialkylcarbamoyl azides in the presence of diisopropylcarbodiimide gives VII[4]. The 1,1-dimethyl-4-isopropyl-5-isopropylimido-1,2,4-triazolidin-3-on-1,2-aminimide VIIa, mp 140-3° (dec) crystallyzes from the photolysis reaction mixture and is thus conveniently obtained. It can also be made, in 93% yield, by heating diisopropylcarbodiimide with IIIa to 65° for 30 minutes. The aminimide VIIa begins to dissociate already in refluxing benzene. It can be used as a source of Me_2N-NCO, but the diisopropylcarbodiimide formed along with the Me_2N-NCO cannot be removed as easily as tBuNCO, the sole by-product in the thermolyses of III. The diisopropylcarbodiimide competes with other addends for the Me_2N-NCO, for example in the preparation of the isothiocyanate adducts VIII :



When the equilibrium mixture is cooled, VIIIa[5] crystallizes and can be removed. By heating the filtrate again, one can obtain VIIIa in 92% yield. Conversely, refluxing VIIIa in benzene with an excess of diisopropylcarbodiimide yields a mixture of VIIa and VIIIa.

The aminimide VIIIa, 1,1,4-trimethyl-1,2,4-triazolidin-3-on-5-thion-1,2-aminimide[5], mp 148° (dec) has carbonyl absorption at 1710 cm^{-1} ($CHCl_3$), nmr signals at δ3.42 (s, 6H) and δ3.38 (s, 3H) and a parent m/e of 159. The mass spectrum shows losses of MeNCS, MeNCO, NCO, and Me_2N_2 -- a pattern very similar to that obtained from the aminimides II (X = O). The chemical proof of the structe of the aminimides VIII, and their reactions, will be reported separately.

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References and Notes

1) W. Lwowski, R. DeMauriac, T.W. Mattingly, Jr., and E. Scheiffele, *Tetrahedron Letters*, 3285 (1964).

2) W.S. Wadsworth and W.D. Emmons, *J. Org. Chem.*, **32**, 1279 (1967).

3) K. Seckinger, *Helv. Chim. Acta*, **56**, 2061 (1973).

4) W. Lwowski, R. DeMauriac, R.A. Murray, and L. LÜnow, *Tetrahedron Letters*, 425 (1971).

5) All new compounds reported gave satisfactory elemental analyses for C, H, and N.

6) We are indebted to Mrs. L. LÜnow for the photochemical experiments.