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REACTION OF t-BUTYL ISOCYANIDE WITH HYDROGEN CHLORIDE

J. Honzl and P. Křivinka

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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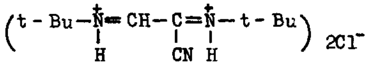
Primary and secondary alkyl isocyanides and phenyl isocyanide react with hydrogen chloride to compounds the structure of which was proved, several years ago, to be Ia-b (1). This reaction is the only known example of oligomerization of isocyanides by acid species where C-N-addition has been proved; oligomerization of isocyanides by $BF_3.OEt_2$ (2a,b) or acyl chlorides(2b) proceeds by the C-C-addition.

We felt that it might be interesting to verify if this reaction occurs also with t-butyl isocyanide. The tertiary isocyanides are known to undergo some specific reactions with acid species which may be explained by the tendency to split off the tertiary carbonium ion. For example, dimerization of t-butyl isocyanide by catalytic amounts of $BF_3.OEt_2$ leads to 2-t-butylimino-3,3-dimethyl butyronitrile (2a,b), and in the reaction of the same isocyanide with cyclic unsaturated ketones and $BF_3.OEt_2$ (3), ketone nitriles or enolether nitriles are formed.

By the reaction of t-butyl isocyanide with hydrogen chloride we obtained a colourless substance which, in analogy to the compounds of type I, reacted with water, had no definite melting point and could not be recrystallized. The same product was obtained by the reaction of t-butyl formamide with carbonyl chloride (identity of both products was proved by the ir spectra). The analysis, spectra and reactions of this compound are consistent with structure II.

$$\left(R-\underset{H}{\overset{+}{N}}=CH-\underset{R}{N}-CHCl_2\right)Cl^- \rightleftharpoons \left(R-\underset{H}{\overset{+}{N}}=CH-\underset{R}{\overset{+}{N}}=CHCl\right)2Cl^-$$

Ia Ib



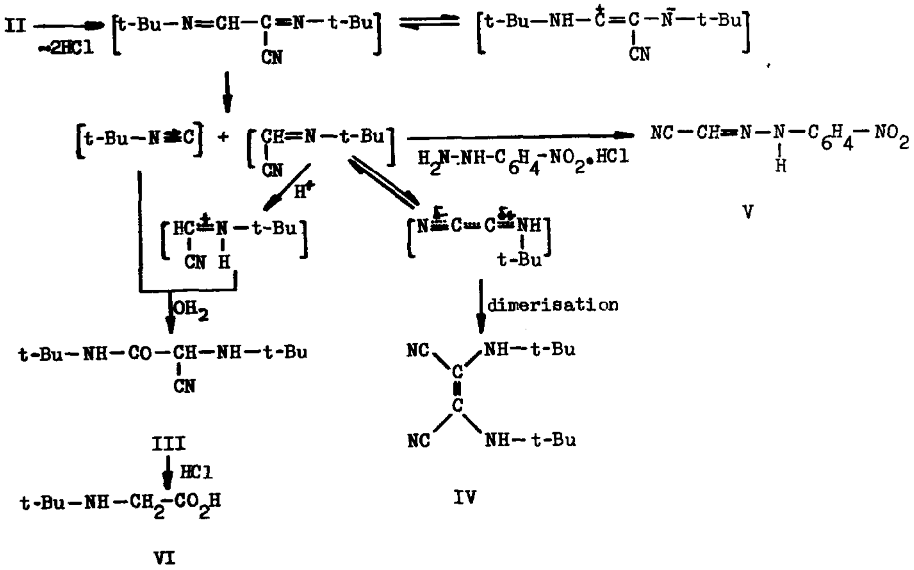
$$\left(t\text{-}Bu-\underset{H}{\overset{+}{N}}=CH-\underset{CN}{C}=\underset{H}{\overset{+}{N}}-t\text{-}Bu\right)2Cl^-$$

II

The nmr spectrum contains, in addition to the peak of the protons in the t-butyl groups (τ 8,47), two peaks (τ +2,25 and τ -0,68) with an intensity ratio of 1:2. The former was assigned to the proton in the methine group, the latter to the protons in the NH-groups. The ir spectrum contains a strong nitrile band at 2208cm^{-1}. The C-N double bond absorption which in compounds of type I is expected to occur at about 1700 cm^{-1}, is shifted to 1615 cm^{-1}, indicating the presence of a different C-N double bond system. In the mass spectrum of II a very intensive molecular ion of deprotonated II with mass 193 was found.

Hydrolysis of II produces t-butylamino cyanoacetic acid t-butyl amide (III)(m.p. 67,5°C) and a small amount of cis-1,2-di-t-butylamino-1,2-dicyanoethylene (IV)(m.p. 77°C). When the hydrolysis was carried out in the presence of p-nitrophenylhydrazine hydrochloride, cyanoformaldehyde p-nitrophenylhydrazone (V) (4) was formed. The structure of III was proved by its hydrolysis and decarboxylation to t-butyl glycine (VI), the structure of IV by the ir and nmr spectra. The nmr spectrum of IV contains the peak of the t-butyl protons (τ 8,69) and the peak at τ 6,24 assigned to the protons in the NH groups. The ir spectrum has a strong nitrile band (ν 2210 cm^{-1}), NH absorption (ν 3370 cm^{-1}) and a band at ν 1590 cm^{-1} which corresponds to the C-C double bond. The latter was also found in the Raman spectrum. These data suggest the cis configuration for IV. A good analogy is provided by cis-1,2-dimorpholino-1,2-dicyanoethylene which has a similar ir absorption while the trans compound has not (5).

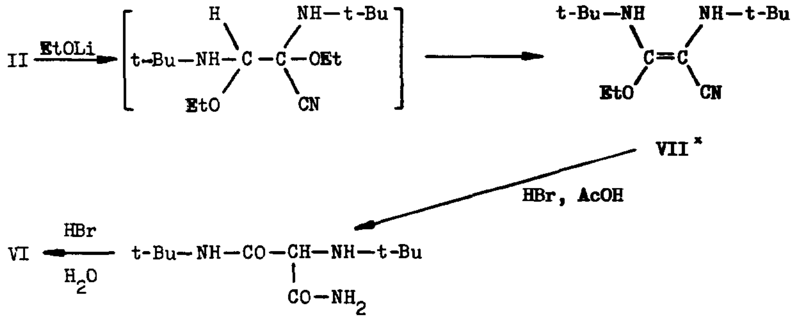
Scheme I



As the first step in the hydrolysis of II (Scheme I) we suggest the hydrolysis to the free base and its decomposition to t-butyl isocyanide and t-butyl iminoacetonitrile. Formation of IV can be explained by dimerization of t-butyl iminoacetonitrile. Similarly, cis-1,2-diamino-1,2-dicyanoethylene is formed by dimerization of the very reactive iminoacetonitrile (stable at temperatures below -160°C) which has (according to spectral data) carbene structure (6). III is formed by reaction of t-butyl isocyanide with t-butyl iminoacetonitrile and water. We regard it as a Ugi-type reaction (7) which can be carried out in diluted mineral acid (8). An alternative mechanism, supposing a reaction of the proton and hydroxyl ion with a tautomer dipolar form of deprotonated II, is also possible.

Reaction of II with lithium ethoxide produced 1,2-di-t-butylamino-1-ethoxy-2-cyanoethylene (VII) (m.p. 48,5°C) in 86% yield. The structure of this compound was proved by stepwise hydrolysis to VIII (m.p. 124,5-125°C) and VI (Scheme II). The ir and Raman spectra are also in agreement with structure VII (ir : 3295 cm^{-1} and 3355 cm^{-1} NH, 2165 cm^{-1} CN; ir and Raman : 1600 cm^{-1} C-C double bond), in the nmr spectrum the very large chemical shift difference between the two NH protons seems rather unusual (nmr : τ 8,10 and τ 4,27 NH, τ 8,88 and τ 8,75 t-Bu, τ 8,57 and τ 5,55 C_2H_5). The formation of VII can be explained by a direct attack of ethoxide ions at II or by the reaction of lithium ethoxide with a tautomer dipolar structure of a deprotonated II.

Scheme II



VIII

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*Configuration on the double bond unknown.

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