Dimerization of *N*-t-Butyliminoacetonitrile

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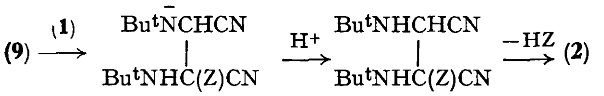
Summary At 130° *N*-t-butyliminoacetonitrile (**1**) under nitrogen in a bomb is transformed into di-t-butylaminomaleonitrile (**2**); and in the presence of potassium cyanide at 25° (**1**) is transformed into 1,2-di-t-butylamino-1,1,2,2-tetracyanoethane (**10**).

As a proposed step in prebiotic polymerization of hydrogen cyanide, the dimerization of iminoacetonitrile $(HCN)_2$ into diaminomaleonitrile $(HCN)_4$ has received considerable attention.[1] To establish a dimerization of iminoacetonitriles, t-butyliminoacetonitrile (**1**)[1] has been thermally transformed into di-t-butylaminomaleonitrile (**2**).

N-t-Butyliminoacetonitrile (**1**) heated under nitrogen in a stainless steel bomb at 130° for 84 h gave a brown solid which was purified by chromatographic separation from a column of silica gel. Benzene eluted colourless needles of di-t-butylaminomaleonitrile (**2**) (17%) m.p. 78—79°[2] λ_{max} 322 nm (ϵ 14,650); *m/e* 220(M^+), 164($M^+ - C_4H_8$), 149($M^+ - C_4H_8, - Me$), 110(M^{++}), 108($M^+ - 2C_4H_8$), 81($M^+ - 2C_4H_8, - HCN$), and 57($C_4H_9^+$). There was excellent agreement with previously reported i.r. and n.m.r. data,[2] and elemental analysis was satisfactory for $C_{12}H_{20}N_4$. The unknown *trans*-isomer was not detected. Elution with ether–benzene (1:1) gave *NN'*-di-t-butylurea (**3**) in low yield; i.r. superposable with the spectrum of an authentic sample.[3] Further elution gave intractable resins.

Ammonia is sufficiently basic to catalyse the tetramerization of hydrogen cyanide into diaminomaleonitrile (**8**) and a similar base catalysed reaction, in the absence of oxygen, is envisaged for the dimerization of t-butyliminoacetonitrile. A trace amount of an impurity, HZ, could initiate an autocatalytic dimerization by adding to (**1**) [equations (1) and (2)].

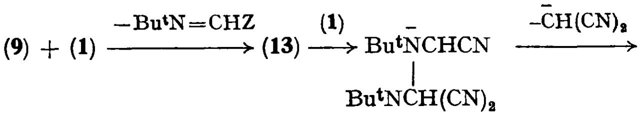
$$(\mathbf{1}) \xrightarrow{HZ} Bu^tNHCH(Z)CN \xrightarrow{(\mathbf{1})} \underset{(\mathbf{9})}{Bu^tNH\overset{-}{C}(Z)CN} + (\mathbf{1})\cdot H^+ \quad (1)$$



$$(\mathbf{9}) \xrightarrow{(\mathbf{1})} \begin{array}{c} Bu^t\overset{-}{N}CHCN \\ | \\ Bu^tNHC(Z)CN \end{array} \xrightarrow{H^+} \begin{array}{c} Bu^tNHCHCN \\ | \\ Bu^tNHC(Z)CN \end{array} \xrightarrow{-HZ} (\mathbf{2}) \quad (2)$$

A similar explanation accounts for the formation of 1,2-di-t-butylamino-1,1,2,2-tetracyanoethane (**10**) in 5% yield from (**1**) and potassium cyanide in DMF at 25° for 19 h. The intermediate, t-butyliminomalononitrile (**11**) was detected by partial hydrolysis during chromatographic separation from silica gel into α-cyano-t-butyliminoacetamide (**12**). Elemental analyses for (**10**) and (**12**) were satisfactory. Further characterization by i.r., u.v., n.m.r., and mass spectral data was completely consistent with each structure.

The formation of *NN'*-di-t-butylurea (**3**) in low yield from (**1**) in both the thermal bomb reaction and the reaction with potassium cyanide tends to confirm intermediates (**9**), (**13**), and (**14**). It is assumed that water is introduced during chromatography. The anions of malononitrile and acetonitrile were not detected.



$$(\mathbf{9}) + (\mathbf{1}) \xrightarrow{-Bu^tN=CHZ} (\mathbf{13}) \xrightarrow{(\mathbf{1})} \begin{array}{c} Bu^t\overset{-}{N}CHCN \\ | \\ Bu^tNCH(CN)_2 \end{array} \xrightarrow{-\overset{-}{C}H(CN)_2}$$

$$Bu^tNHC{=}NBu^t \xrightarrow{-HCN} Bu^tN{=}C{=}NBu^t \xrightarrow{H_2O} \underset{(\mathbf{3})}{Bu^tNHCONHBu^t}$$

$$(\mathbf{14}) + (\mathbf{1}) \xrightarrow[H_2O]{\overset{-}{C}H_2CN \atop -HCN} (\mathbf{3})$$

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[1] J. H. Boyer and H. Dabek, *Chem. Comm.*, 1970, 1204 give leading references.

[2] J. Henzl and P. Křivirka, *Tetrahedron Letters*, 1970, 2357.

[3] A. Buhler and H. E. Fierz-David, *Helv. Chim. Acta*, 1943, **26**, 2123, report sublimation without melting under normal pressure and a m.p. 242°, presumably in a sealed tube.