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FREE-RADICAL ATTACK ON ISOCYANIDES: REACTIONS BETWEEN BISTRIFLUOROMETHYLAMINO-OXYL AND T-BUTYL OR TRIFLUOROMETHYL ISOCYANIDE

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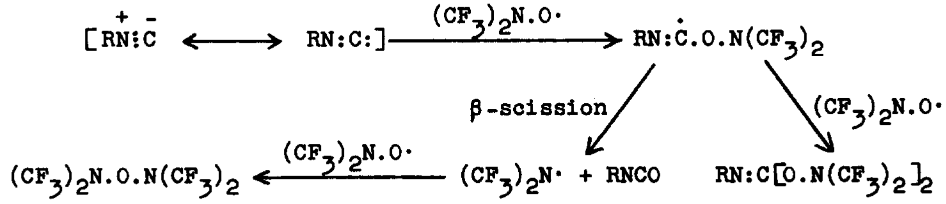
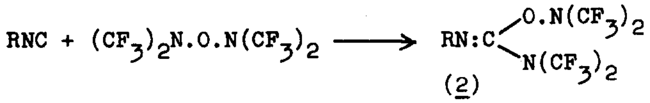
Bistrifluoromethylamino-oxyl reacts readily with isocyanides RNC (R = ^{t}Bu, CF_3) to give $RN{:}C[O.N(CF_3)_2]_2$ and RNCO, and the compounds $RN{:}C[O.N(CF_3)_2][N(CF_3)_2]$ (R = ^{t}Bu) and $RN{:}C[O.N(CF_3)_2].C[O.N(CF_3)_2]{:}N.CF_3$ (R = CF_3) are also produced; perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane), $(CF_3)_2N.O.N(CF_3)_2$, undergoes a novel insertion reaction with ^{t}BuNC to give ${}^{t}BuN{:}C[O.N(CF_3)_2][N(CF_3)_2]$ quantitatively, and reaction of the compound ${}^{t}BuN{:}CCl_2$ with the mercurial $[(CF_3)_2N.O]_2Hg$ provides an alternative synthesis for ${}^{t}BuN{:}C[O.N(CF_3)_2]_2$.

Study of the reaction of bistrifluoromethylamino-oxyl with isocyanides RNC (R = ^{t}Bu, CF_3) has extended the somewhat limited knowledge of free-radical reactions of isocyanides[1] and provides novel information pertaining to bistrifluoromethylamino-oxy chemistry, a field currently attracting attention.[2] The main reaction paths are shown in Scheme 1.



(2) (1)

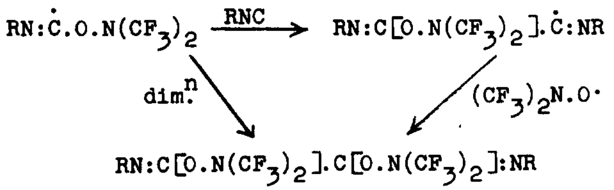
and, when R = ^{t}Bu,



$$\mathrm{RNC} + (\mathrm{CF_3})_2\mathrm{N.O.N(CF_3)_2} \longrightarrow \mathrm{RN{:}C}\begin{cases}\mathrm{O.N(CF_3)_2}\\ \mathrm{N(CF_3)_2}\end{cases}$$

(2)

and, when R = CF_3,



$$\begin{tikzcd}
\mathrm{RN{:}\dot{C}.O.N(CF_3)_2} \arrow[r, "\mathrm{RNC}"] \arrow[dr, "\mathrm{dim^n}"'] & \mathrm{RN{:}C[O.N(CF_3)_2].\dot{C}{:}NR} \arrow[d, "(\mathrm{CF_3})_2\mathrm{N.O\cdot}"] \\
& \mathrm{RN{:}C[O.N(CF_3)_2].C[O.N(CF_3)_2]{:}NR}
\end{tikzcd}$$

(4)

SCHEME 1

R = ^{t}Bu. Storage of an equimolar mixture of t-butyl isocyanide and bistrifluoromethylamino-oxyl at room temperature for 3 days yields t-butyl isocyanate (50%), the new imine $^t\mathrm{BuN{:}C[O.N(CF_3)_2][N(CF_3)_2]}$ (47%), and a trace (1%) of the known[3] N-O-N compound $(\mathrm{CF_3})_2\mathrm{N.O.N(CF_3)_2}$ (3). With a reactant ratio $[^t\mathrm{BuNC{:}(CF_3)_2N.O\cdot}]$ of 1:2 (0 °C for 2 days), the yield of t-butyl isocyanate increases to 60% and another new imine, $^t\mathrm{BuN{:}C[O.N(CF_3)_2]_2}$ (1; R = ^{t}Bu) (17%), is obtained in addition to products (2; R = ^{t}Bu) (21%) and (3) (47%). A further increase in the proportion of the oxyl reactant $[^t\mathrm{BuNC{:}(CF_3)_2N.O\cdot}$ = 1:4; room temperature, 3 days] scarcely affects the yield of t-butyl isocyanate (61%) or of compound (3) (44% based on 53% recovery of the oxyl), but it causes an increase in the yield of compound (1; R = ^{t}Bu) (28%) at the expense of (2; R = ^{t}Bu) (11%). These facts, in conjunction with the observations that (i) $^t\mathrm{BuN{:}C[O.N(CF_3)_2]_2}$, after storage at room temperature for 3 days in the presence of an equimolar amount of t-butyl isocyanide, is recoverable in at least 62% yield, together with ^{t}BuNCO (30%), $^t\mathrm{BuN{:}C[O.N(CF_3)_2][N(CF_3)_2]}$ (3%), and unidentified material including a yellow oil, and (ii) the new type of isocyanide insertion reaction $^t\mathrm{BuNC} + (\mathrm{CF_3})_2\mathrm{N.O.N(CF_3)_2}$ (3) $\longrightarrow$ $^t\mathrm{BuN{:}C[O.N(CF_3)_2][N(CF_3)_2]}$ proceeds cleanly to completion during 2 days at room temperature, are accommodated by Scheme 1.

R = CF_3. Trifluoromethyl isocyanide[4] is more susceptible than its t-butyl analogue towards attack by bistrifluoromethylamino-oxyl, and reaction between approximately equimolar quantities of reactants is complete after 12 hours at room temperature to give the products $CF_3.NCO$ (13%), $(CF_3)_2N.O.N(CF_3)_2$ (3) (12%), $CF_3.N:C[O.N(CF_3)_2]_2$ (27%), and $CF_3.N:C[O.N(CF_3)_2].C[O.N(CF_3)_2]:N.CF_3$ (52%). The greater reactivity of trifluoromethyl isocyanide and the formation of (4; R = CF_3) at the expense of the expected compound (2; R = CF_3) can be associated with the greater carbenoid character of trifluoromethyl isocyanide arising from de-emphasis of the dipolar canonical form owing to the powerful -I effect of a CF_3 group, increased ease of radical attack on trifluoromethyl isocyanide, and the possibility of the radical dimerisation shown in Scheme 1.

The structures of the compounds of type (1), (2), and (4) were established by elemental analysis and spectroscopic methods (i.r., ^{19}F n.m.r., mass, coupled g.l.c.-i.r., and coupled g.l.c.-mass). Additionally, compound (1; R = ^tBu) was synthesised as follows:

$$^tBuN:CCl_2 \xrightarrow[21\ ^\circ C\ (\text{exothermic})]{[(CF_3)_2N.O]_2Hg\ ^5} {}^tBuN:CCl.O.N(CF_3)_2 \xrightarrow[21\ ^\circ C]{[(CF_3)_2N.O]_2Hg} (1;\ R = {}^tBu)$$

References

[1] 'Isonitrile Chemistry', ed. I. Ugi, Academic Press, New York and London, 1971, p. 84.

[2] For recent reviews see D.P. Babb and J.M. Shreeve, *Intra-Science Chemistry Reports*, 1971, 5, 55, and R.E. Banks and M.G. Barlow, 'Fluorocarbon and Related Chemistry' (Vol. 1), Specialist Periodical Report, The Chemical Society, London, 1971.

[3] See, for example, R.E. Banks, R.N. Haszeldine, and M.J. Stevenson, *J.Chem.Soc.(C)*, 1966, 901; R.N. Haszeldine and A.E. Tipping, *ibid.*, p. 1236; R.E. Banks, R.N. Haszeldine, and T. Myerscough, *J.C.S. Perkin I*, 1972, paper no. 2/178, in press.

[4] R.E. Banks, R.N. Haszeldine, M.J. Stevenson, and B.G. Willoughby, *J.Chem.Soc.(C)*, 1969, 2119.

[5] Prepared *in situ* from $(CF_3)_2N.O\cdot$ and Hg; H.J. Emeléus, J.M. Shreeve, and P.M. Spaziante, *J.Chem.Soc.(A)*, 1969, 431.