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POLYMERIZATION, OXYGENATION AND ISOMERIZATION OF ISOCYANIDES UNDER IRRADIATION

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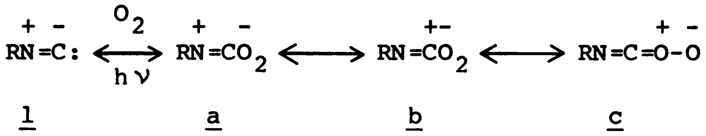
Irradiation in the presence of triplet oxygen polymerized both 2,4-dimethyoxyphenyl and cyclohexyl isocyanide and photoautoxidized each into the corresponding isocyanate. The aryl, but not the alicyclic, isocyanide also photoisomerized into a cyanide. The consumption of an isocyanide was enhanced in the presence of certain aromatic hydrocarbons, e.g., naphthalene and phenanthrene, but was diminished in the presence of pyrene. Two bisisocyanides were unaffected by the presence of oxygen during irradiation.

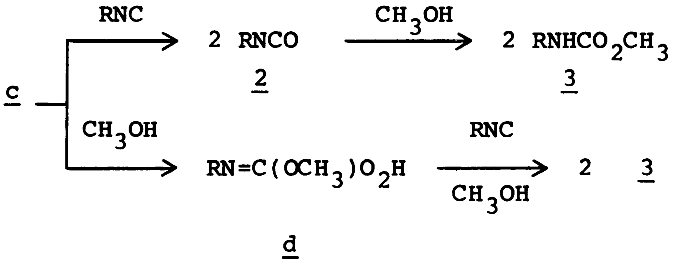
Carbenoid nucleophilicity accounted for sulfurization of both an isocyanide and carbon monoxide and selenization of an isocyanide,[1] but it did not facilitate oxygenation of either compound in its ground state.[2] An isocyanide was oxidized into an isocyanate by silver or mercuric oxide, ozone, peracids, metal-oxygen complexes such as $Ni(RNC)_2O_2$ and $Pt(PPh_3)_3O_2$, nitric oxide, and by either dimethyl sulfoxide or pyridine-N-oxide in the presence of halogens.[2a] Photoisomerization of certain aryl isocyanides into cyanides has been described.[3]

An electron transfer from an isocyanide to oxygen can account for an isocyanate oxide c, one form of a proposed intermediate for the peroxidations 1 → 2, and/or 1 → methyl carbamate 3 in the presence of methanol.[4,5] Polymerization[6] 1 → 4 was presumably initiated by an electrophilic attack from the zwitterionic peroxide b upon the isocyanide 1. Isomerization of an isocyanide into a cyanide 5 was a competitive reaction.[3]

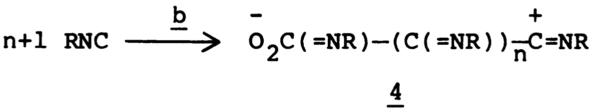


$$\underset{\underline{1}}{\overset{+\ -}{\mathrm{RN{=}C{:}}}} \underset{h\nu}{\overset{O_2}{\longleftrightarrow}} \underset{\underline{a}}{\overset{+\ \ -}{\mathrm{RN{=}CO_2}}} \longleftrightarrow \underset{\underline{b}}{\overset{+-}{\mathrm{RN{=}CO_2}}} \longleftrightarrow \underset{\underline{c}}{\overset{+\ -}{\mathrm{RN{=}C{=}O{-}O}}}$$

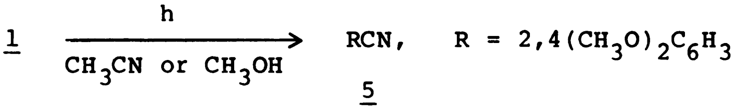
R = 2,4$(CH_3O)_2C_6H_3$, Cyclo-C_6H_{11}



$$\underline{c}\ \begin{cases} \xrightarrow{\mathrm{RNC}} 2\ \underset{\underline{2}}{\mathrm{RNCO}} \xrightarrow{\mathrm{CH_3OH}} 2\ \underset{\underline{3}}{\mathrm{RNHCO_2CH_3}} \\ \xrightarrow{\mathrm{CH_3OH}} \underset{\underline{d}}{\mathrm{RN{=}C(OCH_3)O_2H}} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{RNC}} 2\ \ \underline{3} \end{cases}$$

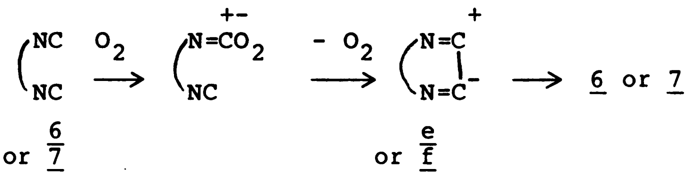


$$\mathrm{n{+}1\ RNC} \xrightarrow{\underline{b}} \underset{\underline{4}}{\overset{-}{\mathrm{O_2}}\mathrm{C({=}NR){-}(C({=}NR))_n{-}}\overset{+}{\mathrm{C}}\mathrm{{=}NR}}$$



$$\underline{1} \xrightarrow[\mathrm{CH_3CN\ or\ CH_3OH}]{\mathrm{h}} \underset{\underline{5}}{\mathrm{RCN}},\quad \mathrm{R} = 2,4(\mathrm{CH_3O})_2\mathrm{C_6H_3}$$

An apparent resistance to photoautoxidation by 2,2'-diisocyanobiphenyl 6 ((o-$CNC_6H_4)_2$)[7] and by the dimethyl ether 7 ((p-$CH_3OC_6H_4CH{=}CNC)_2$)[8] of xanthocillin was attributed to a displacement of oxygen as an intramolecular isocyanide "dimer" e or f was produced.



The aryl isocyanide (0.1 M in acetonitrile) was consumed (27%), and the aryl isocyanate (11%), a polymer (73%) and the aryl cyanide (10%) were produced by irradiation (254 or 300 nm) for 24 h in the presence of a stream of oxygen.[9] A similar treatment consumed (18%) the alicyclic isocyanide as the alicyclic isocyanate (13%) and a polymer were produced; however the alicyclic isocyanide was quantitatively recovered from irradiation at 300 or 350 nm.[9] In the absence of irradiation each isocyanide was nearly quantitatively recovered.

When methanol replaced acetonitrile, irradiation afforded (a) methyl 2,4-dimethoxyphenylcarbamate (4%) and the corresponding aryl cyanide (33%) as the aryl isocyanide was consumed (12%) and (b) cyclohexylcarbamate (4%) as the alicyclic isocyanide was consumed (35%).[9] In the absence of oxygen both isocyanides were polymerized; and as the aryl isocyanide was consumed (15%) photoisomerization gave the cyanide (30%)[3] but a photoisomerization of cyclohexyl isocyanide did not occur.[10]

Singlet oxygen, from the peroxide of 9,10-diphenylanthracene [11] was unreactive and each isocyanide was quantitatively recovered. This was in agreement with the inability of β-carotene[12] to quench photoautoxidation of either the aryl or the alicyclic isocyanide.

Addition of phenanthrene (0.05 M) increased the consumption of the aryl isocyanide to 46% (irradiation at 300 nm) and of the alicyclic isocyanide to 70% (irradiation at 350 nm); a similar effect from naphthalene (0.1 M) on irradiation (300 nm) of the aryl isocyanide was obtained. Although there was an accompanying increase in the production of the alicyclic isocyanate from trace amounts to 18%, there was a decrease in the production of the aryl isocyanate and cyanide. Addition of pyrene (0.01 M) decreased the consumption of the aryl isocyanide to 7%. A careful search for products revealed no chemical reaction between an added hydrocarbon and either isocyanide. Further investigation of this unaccounted for hydrocarbon effect is planned.

References and Notes.

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9. Except for polymers, each product was identified by direct comparison with the authentic compound. The progress of each reaction was monitored by the development of absorption at 1755-1670 cm^{-1} (-N=C<) for the polymer and near 2250 cm^{-1} (NCO) for the isocyanate. Each polymer gradually coated the wall of the quartz tube and darkened the solution.

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