Journal of Fluorine Chemistry, *11* (1978) 567–572
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Received: October 20, 1977

PRELIMINARY NOTE

The reactions of the stable azomethinimine 2-(5,5-dimethyl-3,3-bistrifluoromethyl-1-pyrazolin-1-ylio)-1,1,1,3,3,3-hexafluoropropan-2-ide with compounds containing the N-O bond

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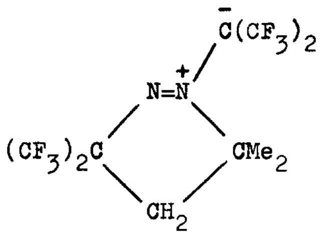
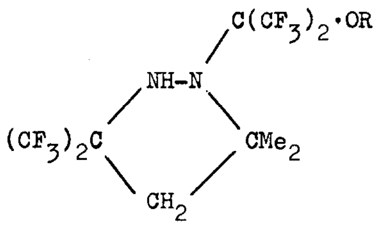
The azomethinimine (I), prepared by the reaction of hexafluoroacetone azine with 2-methylpropene at room temperature,[1,2] has been reported[3] to give the adducts (II) and (III) on treatment with alcohols and phosphites, respectively. Reaction of (I) with a variety of alkenes affords criss-cross adducts (IV);[2,4] acetylenes react analagously.[4]



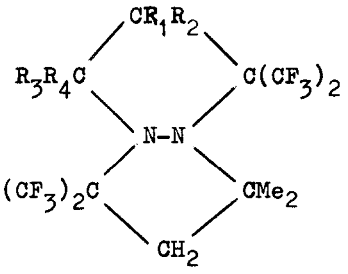
(I)



(II)

$(CF_3)_2C{=}N\cdot CMe_2\cdot CH_2\cdot C(CF_3)_2\cdot N{=}PR_3$

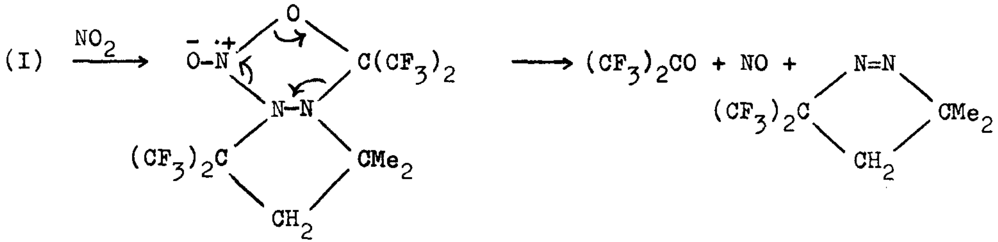
(III)



(IV)

In the present work the reactions of various compounds containing the N-O bond, i.e. NO_2, NOCl, R_FNO ($R_F = CF_3$ and $CF_3.CF_2.CF_2$), $(CF_3)_2N{\cdot}O{\cdot}$, and $(CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$, with the propanide (I) have been investigated.

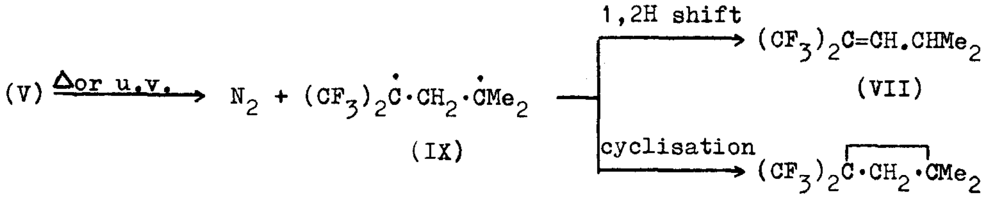
Treatment of (I) with nitrogen dioxide at room temperature gave the Δ^1-pyrazoline (V) (98%) and equimolar quantities of nitric oxide and hexafluoroacetone. These products are considered to be formed via decomposition of an intermediate adduct (VI), i.e.



(VI)

(V)

Static pyrolysis of the pyrazoline (V) at 210° (22 h) afforded nitrogen (99%), alkene (VII) (85%), and cyclopropane (VIII) (14%) while photolysis (ca. 40°, 25 h) gave unchanged (V) (57% recovered), nitrogen (100%), (VII) (12%), and (VIII) (88%). The products are consistent with the formation of an intermediate diradical (IX) analagous to those postulated for thermal[5] and photochemical[6] decompositions of other Δ^1-pyrazolines, i.e.

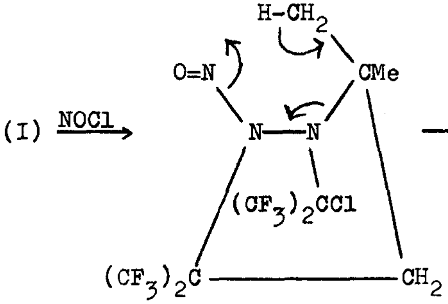


(IX)

(VII)

(VIII)

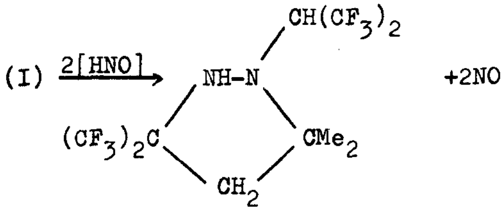
The reaction of (I) with nitrosyl chloride (ca. 1:1 molar ratio) at room temperature (7 days) gave unchanged (I) (2% recovered); hexafluoroacetone (2.5%), pyrazoline (V) (2.5%), diene (X) (7%), chlorodiene (XI) (66%), and dihydropyrazoline (XII) (23%) based on (I) reacted; and nitric oxide (96%) and hydrogen chloride (24%) based on NOCl. The reduced compound (XII) was an unexpected product and it is postulated that it was formed, together with the other major products, *via* decomposition of the intermediate 1:1 adduct (XIII), *i.e.*



$\longrightarrow [HNO] + (CF_3)_2CCl{\cdot}N{=}N{\cdot}C(CF_3)_2{\cdot}CH_2{\cdot}CMe{=}CH_2$

(XIII)

(XI)

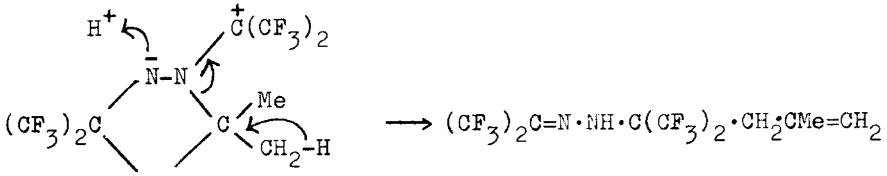


(XII)

$$NOCl + [HNO] \longrightarrow HCl + 2NO$$

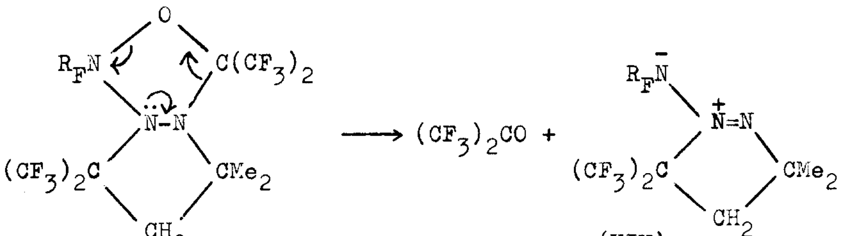
It is possible that compound (XI) and hydrogen chloride are formed to some extent by reaction of (I) with chlorine (present in the NOCl from the equilibrium $2NOCl \rightleftharpoons 2NO + Cl_2$). Of the remaining products hexafluoroacetone and (V) probably arise by reaction of

(I) with nitrogen dioxide impurity in the nitrosyl chloride (prepared by the reaction KCl + $2NO_2 \longrightarrow NOCl + KNO_3$) while diene (X) is probably formed by acid-catalysed rearrangement of (I), i.e.

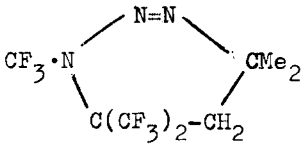


(X)

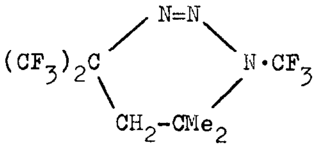
A 1:1 molar mixture of (I) and trifluoronitrosomethane maintained at room temperature (21 days) gave hexafluoroacetone (97%) and a solid (m.p. 31-32°) (97%) shown to have the molecular formula $C_8H_8F_9N_3$ by microanalysis and mass spectrometry. The solid exhibited a strong absorption at 1500 cm^{-1} in its i.r. spectrum of comparable intensity to that (1510 cm^{-1}) observed in the spectrum of (I) and assigned to the azomethinimine system. On this evidence the product is tentatively identified as the azimine[7] (XIV; $R_F = CF_3$) a member of a hitherto unknown class of 1,3-dipolar compounds. The possibility that the product was the rearranged six-membered ring compound (XV) or (XVI) was discounted on the basis of the mass spectrum which did not show a strong ion peak at m/e 289 $(\underline{M}-N_2)^+$. An analagous reaction occured on treatment of (I) with heptafluoronitrosopropane to give hexafluoroacetone (83%) and a compound $C_{10}H_8F_{13}N_3$ (82%) tentatively assigned structure (XIV; $R_F = CF_3\cdot CF_2\cdot CF_2$).



(XIV)

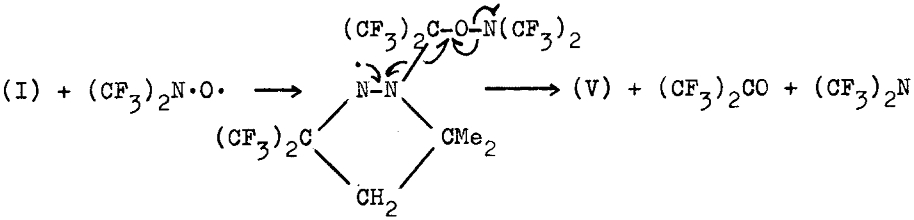


(XV)



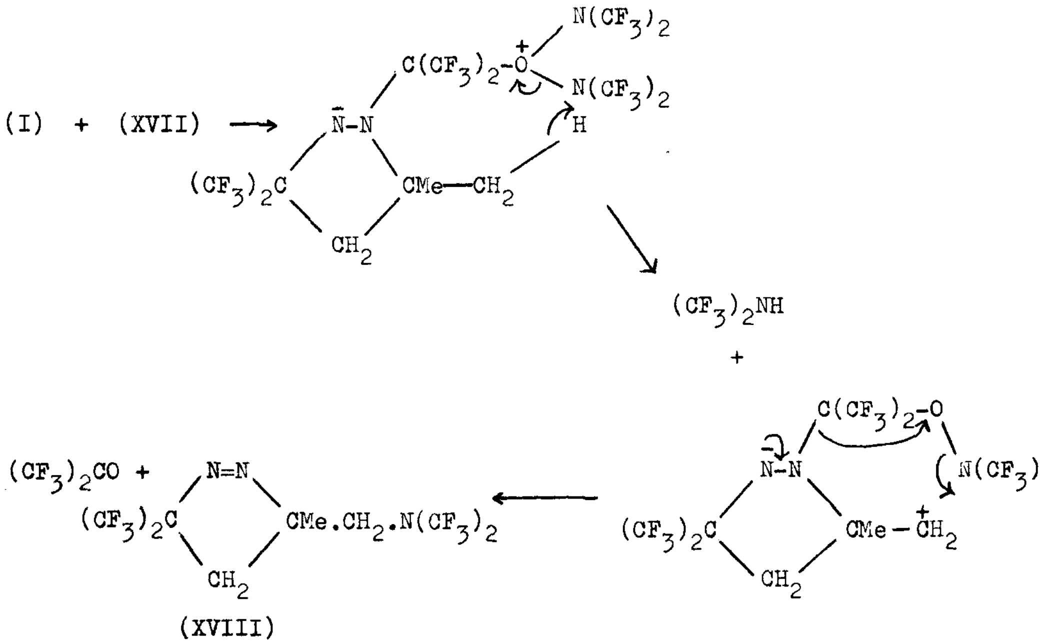
(XVI)

The reaction of (I) with the oxyl $(CF_3)_2N{\cdot}O{\cdot}$ (20°, 12 days) afforded <u>NN</u>-bistrifluoromethylamine (22%), <u>NN</u>-bistrifluoromethylhydroxylamine (6%), and the oxadiazapentane (XVII) (50%) based on oxyl, together with hexafluoroacetone (100%), the Δ^1-pyrazoline (V) (71%) and, surprisingly, the substituted Δ^1-pyrazoline (XVIII) (19%) based on (I); several minor unidentified compounds with longer g.l.c. retention times were also formed. These products prompted an investigation of the reaction of the oxadiazapentane (XVII) with (I) which afforded the pyrazolines (V) (35%) and (XVIII) (65%). We suggest that the major products from these reactions may be formed as follows:



$$(CF_3)_2N{\cdot} + (CF_3)_2N{\cdot}O{\cdot} \longrightarrow (CF_3)_2N{\cdot}O{\cdot}N(CF_3)_2$$

(XVII)



All the identified compounds gave satisfactory spectral and elemental analysis data.

We thank the S.R.C. for a grant (to D.B.).

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