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REACTIONS OF 2,2,2-TRIFLUORODIAZOETHANE WITH CARBON-NITROGEN AND CARBON-OXYGEN MULTIPLE BONDS

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SUMMARY

2,2,2-Trifluorodiazoethane reacts with trifluoroacetonitrile in the dark at room temperature to give a 2-(2,2,2-trifluoroethyl)-4, 5-bis(trifluoromethyl)triazole, the 1,2,3-triazole structure being preferred to the 1,2,4-isomer on the basis of the ^{19}F n.m.r. spectrum. The diazoethane reacts more slowly with trichloroacetonitrile, again forming the N-alkylated triazole even in the presence of an excess of the nitrile. No identifiable adduct resulted with acetonitrile. Hexafluoroisopropylideneimine is first N-alkylated and then undergoes addition to form 1-(2,2,2-trifluoro-1-trifluoromethyl)ethyl-4,5-bis(trifluoromethyl)-Δ^2-1,2,3-triazoline, but N-methylhexafluoroisopropylideneimine failed to react. Trifluoroacetaldehyde and trichloroacetaldehyde give mixtures of the ketone (formed by insertion of the CF_3CH group into the aldehyde C-H bond) and the cis- and trans-oxirans, apparently via a β-hydroxydiazoalkane.

INTRODUCTION

Although the addition of diazoalkanes to carbon-carbon multiple bonds has been well known for many years [1], the reaction with carbon-nitrogen multiple bonds has been less widely studied. Early workers reported that alkyl nitriles showed no reaction with diazomethane, although cyanogen and cyanogen halides gave the 1,2,3-triazoles [2], and subsequently the reaction with cyanogen bromide was reinvestigated [3]. The reaction of diazomethane with aromatic Schiff bases has been found to give 1,2,3-triazolines [4], and more recently the reaction of diazomethyltrimethylsilane with trifluoroacetonitrile [5], and of diazomethane with some $R_FN{:}CF$- compounds [6] have also been reported.

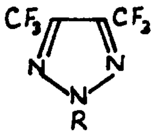
In contrast to these addition reactions, the more widely studied reactions of diazoalkanes with aldehydes and ketones usually result in insertion into the OC-H or OC-C bond and/or oxiran formation. The latter reaction is favoured by electron-withdrawing substituentson the carbonyl group [7], but recently the formation of 1,3,4-oxadiazolines from hexafluoroacetone and aryldiazomethanes has been related to electron withdrawal by the CF_3 groups [8].

The reaction of 2,2,2-trifluorodiazoethane with some nitriles, imines, and aldehydes containing electron-withdrawing groups complement our study of the reactions of this diazoalkane with carbon-carbon multiple bonds [9,10], and are now reported.

RESULTS AND DISCUSSION

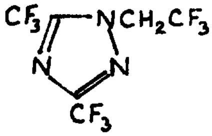
Reactions with carbon-nitrogen multiple bonds.

After two days at room temperature, a mixture of 2,2,2-trifluorodiazoethane and trifluoroacetonitrile gave nitrogen (45%) and an 84% yield of the 2-trifluoroethyl-1,2,3-triazole (Ib) was obtained, presumably *via* addition to the $C\equiv N$ bond and tautomeric shift to give the triazole (Ia), followed by reaction of (Ia) with a second mole of the diazoethane to give (Ib). N-Alkylation was apparently complete in spite of the presence of an excess of nitrile.

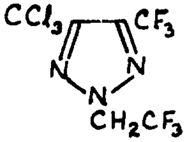


(Ia) R = H

(Ib) R = CH_2CF_3



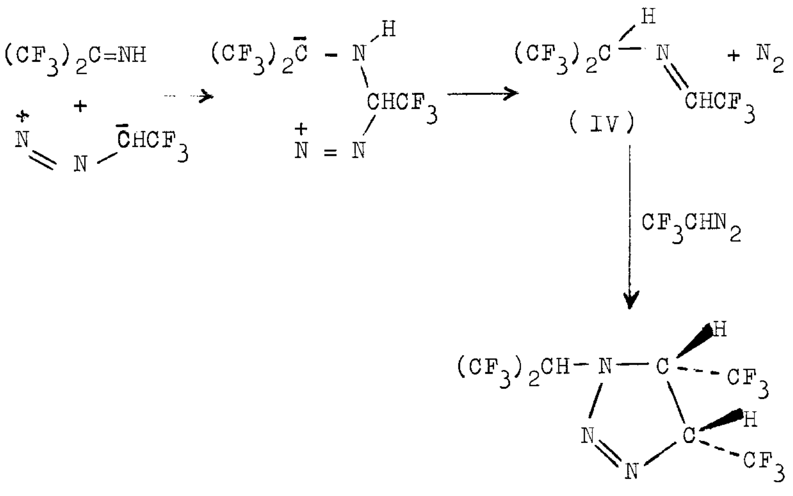
(II)



(III)

The symmetrical structure (Ib) was preferred to the 1,2,4-triazole (II) since the ^{19}F n.m.r. spectrum showed only one sharp singlet for the two ring CF_3 groups. Trichloroacetonitrile similarly gave a high yield of the N-trifluoroethyl triazole, again formulated as the 1,2,3-isomer (III), but in accord with the earlier work with diazomethane [2], acetonitrile gave only a low yield of unidentifiable material, the diazoethane being recovered from the reaction mixture in 44% yield after one year at room temperature.

Hexafluoroisopropylideneimine reacted readily with the diazoethane, and after 15 days, a 19% yield of the azapent-2-ene (IV), and a 55% yield of the triazoline (V), formed by 1,3-dipolar addition of the diazoalkane to (IV), were obtained. The n.m.r. spectra of (V) showed three distinct trifluoromethyl groups, and also strong (8.2 Hz) H-H coupling between the ring hydrogens (assigned the <u>cis</u> configuration in view of the magnitude of the coupling constant), neither of which would be expected for the alternative 1,2,4-triazoline. N-Methylhexafluoroisopropylideneimine failed to react with the diazoethane in the dark, indicating that the initial step in the above reaction is probably nucleophilic attack on the imine by the carbon atom of the diazoalkane, followed by hydrogen migration and loss of nitrogen from the zwitterion to give (IV).



(V)

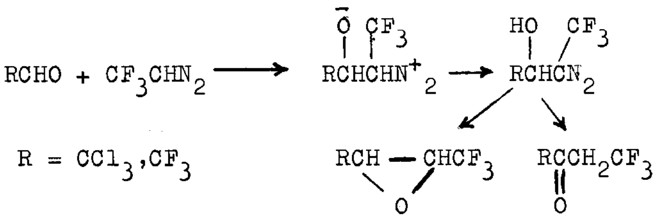
The formation of the 1,2,3-triazoles and -triazoline is in accord with the rather limited studies of the reactions of diazomethane with cyanogen and with Schiff bases [2-4] and also with products obtained recently by Coe and Holton from the reaction of diazomethane with undecafluoro-2-azahex-2-ene and with nonafluoroazacyclohex-1-ene [6], but is contrary to the idea of maximum gain in σ-bond energy, which predicts the formation of the 1,2,4-isomer. The present work does not, however, provide evidence that these reactions are concerted, and it is possible, as Huisgen has suggested for other cases where the maximum gain in σ-bond energy does not apply [11], that we are dealing here with two-step reactions.

Reactions with carbon-oxygen double bonds

2,2,2-Trifluorodiazoethane appeared to react only slowly in the dark with trifluoroacetaldehyde, to give a mixture of 1,1,1,4,4,4-hexafluorobutan-2-one (5%) and the cis- and trans-oxirans (63%), but it was not possible to decide from the n.m.r. spectra whether the more abundant oxiran was the cis- or the trans-isomer. The pale yellow involatile residue appeared from the i.r. spectrum to contain both hydroxyl and diazo groups.

The reaction with trichloroacetaldehyde also appeared to be slow, and after six weeks, nitrogen (50%) and the excess of trichloroacetaldehyde were isolated, together with an involatile mixture, inseparable by distillation, which showed ketone, oxiran, hydroxyl, and diazo group absorptions in its i.r. spectrum. The ^{19}F n.m.r. spectrum showed a triplet (+14.6 p.p.m.,8.6 Hz) assigned to 1,1,1-trichloro-4,4,4-trifluorobutan-2-one, a doublet (+4.4 p.p.m., 4.1 Hz) and distorted doublet of doublets (+16.6 p.p.m.) assigned to cis- and trans- 2-trichloromethyl-3-trifluoromethyloxiran and a sharp singlet (+20.7 p.p.m.). When the sample was re-examined twelve months later, the singlet had diminished in intensity, and the other three ^{19}F bands had increased, but in different proportions, indicating that the material giving rise to the ^{19}F n.m.r. singlet is a precursor of both the ketone and the oxiran isomers. After the sample had been kept at 55 °C for three days, the singlet had completely disappeared, as had the hydroxyl and diazo-group i.r. bands, and nitrogen was collected.

The evidence thus suggests that the reaction of 2,2,2-trifluorodiazoethane with trichloro-and trifluoroacetaldehyde proceeds via the formation of a reasonably stable β-hydroxy-diazoalkane which can decompose to give either the ketone or the oxirans.



cis and trans

An analogous, but much less stable, intermediate has been trapped by means of its reaction with dimethyl acetylenedicarboxylate from the reaction of trichloroacetaldehyde with diazo-methane [12], and a series of stable β-hydroxydiazo-compounds has since been obtained by base-catalysed condensation of ethyl diazoacetate with aldehydes [13]. The stability of the β-hydroxydiazo-compounds in the present work presumably results from the electron withdrawing effect of the α-trifluoromethyl group. There was no indication of the formation of an oxadiazoline analogous to those reported by Shimizu and Bartlett [8].

EXPERIMENTAL

The preparation and manipulation of the diazoalkane were as described previously [9]. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer, n.m.r. spectra on a Perkin-Elmer R10 or Varian H.A.100 spectrometer [chemical shifts being positive to low field of external trifluoroacetic acid (^{19}F) or benzene (^{1}H)], and mass spectra on an A.E.I. MS2H spectrometer. Molecular weights determined by mass spectrometry are designed $\underline{M}^+$, those by Regnault's method, $\underline{M}$.

WARNING

Although 2,2,2-trifluorodiazoethane is more stable than ordinary diazoalkanes, stringent safety precautions are necessary at all times. (See ref.10).

Reactions of 2,2,2-Trifluorodiazoethane in the Dark

The reactions were carried out in Pyrex tubes, sealed *in vacuo*, kept in the dark at room temperature, and examined periodically as described previously [10].

(a) With trifluoroacetonitrile

The diazoethane (1.65 g, 15 mmol) and trifluoroacetonitrile (1.85 g, 30 mmol) reacted completely in two days to give nitrogen (0.19 g, 45%), recovered trifluoroacetonitrile (2.12 g, 75%), and 2-(2,2,2-trifluoroethyl)-4,5-bistrifluoromethyl-1,2,3-triazole (nc) (1.82 g, 84% based on initial trifluorodiazoethane), b.p. (isoteniscope) 133 ± 1 °C, ^{19}F n.m.r. +14.9 (t, J($C\underline{F}_3C\underline{H}_2$) 7.5 Hz, 35%) and +5.0 (s, 65%).
Analysis: Found: C, 25.1; H, 0.7; F, 59.6; N, 14.6%.
$C_6H_2F_9N_3$ requires C, 25.3; H, 0.9; F, 60.0; N, 14.5%.

(b) With trichloroacetonitrile

After 3 weeks, the diazoethane (1.65 g, 15 mmol) and trichloroacetonitrile (2.89 g, 20 mmol) gave nitrogen (0.15 g, 36%) and recovered diazoethane (0.24 g, 14%) and nitrile (2.08 g, 72%). Distillation of the residue gave a liquid, b.p. 45 °C/1 mmHg, which crystallised and was identified as 2-(2,2,2-trifluoroethyl)-4-trichloromethyl-5-trifluoromethyl-1,2,3-triazole (nc) (1.75 g, 81% based on diazoethane consumed), m.p. 30 °C, ^{19}F n.m.r. singlet and triplet (J($C\underline{F}_3$-$C\underline{H}_2$) 7.7 Hz) of equal intensity +19.8, +7.7. p.p.m.
Analysis: Found: C, 21.6; H, 0.7; N, 12.7%; $\underline{M}^+$ 321.
$C_6H_2F_6N_3Cl_3$ requires C, 21.4; H, 0.6; N, 12.5%, $\underline{M}$, 321.

(c) With acetonitrile

Acetonitrile (0.62 g, 15.0 mmol) and the diazoethane (1.10 g, 10.0 mmol), after twelve months gave 2,2,2-trifluorodiazoethane (0.48 g, 44%), recovered acetonitrile(0.50 g, 81%), nitrogen (0.15 g, 53%), unidentified volatile material (0.10 g), and a viscous yellow residue (0.48 g) which showed only broad i.r. absorption.

(d) With hexafluoroisopropylideneimine

The diazoethane (1.65 g, 15.0 mmol) and hexafluoroisopropylideneimine (3.30 g, 20 mmol), after 15 days, gave (i) nitrogen (0.25 g, 58%); (ii) 1,1,1,5,5,5-hexafluoro-4-trifluoromethyl-3-azapent-2-ene (nc) (0.75 g, 19%), ^{19}F n.m.r. +2.8 p.p.m. [d, $J(C\underline{F}_3\text{-}C\underline{H})$ 3.0 Hz, 33%] and +5.1 p.p.m. [d, $J(C\underline{F}_3)_2C\underline{H}$ 6.0 Hz, 67%], ^1H n.m.r. -2.7 p.p.m. (septet, 6.0 Hz, 50%) and + 0.9 p.p.m. (q, 3 Hz, 50%). Analysis: Found: C, 24.6; H, 1.1; N, 5.9%; $\underline{M}$, 248. $C_5H_2F_9N$ requires C, 24.3; H, 0.8; N, 5.7%; $\underline{M}$, 247; (iii) recovered hexafluoroisopropylideneimine (2.11 g, 64%); and (iv) white crystalline 1-(2,2,2-trifluoro-1-trifluoromethyl)ethyl-4,5-bis(trifluoromethyl)-Δ^2-1,2,3-triazoline (nc) (1.47 g, 55%, based on initial diazoethane), m.p. 55-56°, ^{19}F n.m.r. +7.5 p.p.m. [2 overlapping doublets, $J((C\underline{F}_3)_2C\underline{H})$ 6.9 Hz, 50%], + 1.0 p.p.m. [distorted d, $J(C\underline{F}_3\text{-}C\underline{H})$ 5.9 Hz, 25%] and +2.4 p.p.m. [distorted d, $J(C\underline{F}_3\text{-}C\underline{H})$ 7.4 Hz, 25%], ^1H n.m.r. -1.55 p.p.m. [d, $J(C\underline{H}\text{-}C\underline{H})$ 8.2 Hz of q $J(C\underline{F}_3\text{-}C\underline{H})$ 7.4 Hz, 4-C$\underline{H}$], -2.58 p.p.m. [d, 8.2 Hz of q $J(CF_3\text{-}CH)$ 5.4 Hz, 5-CH], and -2.1 p.p.m. (septet, J 6.9 Hz). Analysis: Found: C, 23.7, H, 1.0; N, 11.7%. $C_7H_3F_{12}N_3$ requires C, 23.5; H, 0.8; N, 11.8%.

(e) With N-methylhexafluoroisopropylideneimine

The diazoethane (1.65 g, 15.0 mmol) and N-methylhexafluoroisopropylideneimine (3.79 g, 21.1 mmol), after 10 weeks, gave nitrogen (0.09 g, 22%) and recovered imine (3.7 g, 98%) and diazoethane (1.3 g, 80%).

(f) With trifluoroacetaldehyde

After one month, the diazoethane (1.65 g, 15.0 mmol) and trifluoroacetaldehyde (2.94 g, 30.0 mmol) gave nitrogen

(0.29 g, 69%), recovered trifluoroacetaldehyde (1.63 g, 55%), an unidentified pale yellow high-boiling liquid (0.79 g), i.r. 2.87 μm (OH) and 4.71 μm (diazo-group), and a mixture of 1,1,1,4,4,4-hexafluorobutan-2-one (0.12 g, 5% yield based on n.m.r. integration and initial trifluorodiazoethane), i.r. (C=O) 5.60 μm, ^{19}F n.m.r. - 4.3 p.p.m. (s) and +12.80 [t,J(C$\underline{F}_3$ - C$\underline{H}_2$) 8.2 Hz], and *cis*- and *trans*-2,3-bis(trifluoromethyl)oxiran (1.7 g, 63% yield), ^{19}F n.m.r. +1.0 p.p.m. (d, 3.9 Hz, 61%) and +7.8 p.p.m. [deceptively simple $A_3XX'A'_3$ pattern, $|J(AX)+J(AX')|$ 7.3 Hz, 31%]. Analysis: Found, C, 27.0, H, 1.3%; *M*, 178. Calc. for $C_4H_2F_6O$: C, 26.7; H, 1.1%, *M*, 180.

(g) With trichloroacetaldehyde

After 6 weeks, trichloroacetaldehyde (2.95 g, 20.0 mmol) and the diazoethane (1.65 g, 15.0 mmol) gave nitrogen (0.15 g, 50%), unreacted trichloroacetaldehyde (1.1 g, 37%), and a mixture (3 g), b.p. 35 °C/1 mmHg, of 1,1,1-trichloro-4,4,4-trifluorobutan-2-one, *cis* - and *trans*-2-trichloromethyl-3-trifluoromethyloxiran, and a compound tentatively identified as 1,1,1-trichloro-2-hydroxy-3-diazo-4,4,4-trifluorobutane in the ratio 1:2:3:7 from ^{19}F n.m.r. integration. After twelve months in the dark (R.T.) the ^{19}F integration was 2:4:9:3, and after a further 3 days at 55 °C, 2:5:12:0.

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