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REACTIONS OF TETRAFLUOROETHENE OLIGOMERS PART 6. SOME REACTIONS OF 4-DIAZO-1,1,1,2,2-PENTAFLUORO-3-PENTAFLUOROETHYL-3-TRIFLUOROMETHYLBUTANE*

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SUMMARY

The isocyanate R_fCH_2NCO ($R_f=CF_3(C_2F_5)_2C$) reacts under strongly acidic conditions to form the salt $R_fCH_2NH_3^{(+)}HSO_4^{(-)}$(1) which yields, on treatment with sodium nitrite the diazaoalkane R_fCHN_2 (3). Dissolution of (1) in D.M.S.O. gives, by a remarkable decomposition reaction, the alkane R_fH (2). Reaction of (3) with excess sodium nitrite affords the isocyanate R_fNCO (4) which is stable to water,but which reacts with ammonia to give the urea $R_fNHCONH_2$ (5); this latter was not readily hydrolysed .Photolysis of (3) yields the diazadiene $R_fCH=N-N=CH\ R_f$ (7). Thermolysis of (3) alone afforded the diazadiene (7), but reaction in the presence of copper (II) perchlorate afforded (7) and the aldehyde R_fCHO (6)

INTRODUCTION

As part of our continuing study of the reactions of tetrafluoroethene oligomers and their derivatives we now report an improved synthesis and some reactions of 4-diazo-1,1,1,2,2-pentafluoro-3-pentafluoroethyl-3-

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*Part 5. P.L. Coe, A. Sellars, J.C. Tatlow, H.C. Fielding and G. Whittaker J. Fluorine Chem., 32 (1986) 151.

trifluoromethylbutane (3). Although there is an extensive chemistry of hydrocarbon diazoalkane derivatives, which has been comprehensively reviewed [1], relatively few of the corresponding polyfluoro derivatives are known, mainly due to the difficulty of obtaining starting materials. The chemistry of some of those derivatives e.g. CF_3CHN_2 which have been made, has been reviewed [2]; in general the reactions are what would have been predicted. The synthesis of these diazoalkanes usually occurs by diazotisation of the corresponding amine. The loss of a proton from the resulting diazonium salt is favoured rather than loss of the diazo group to give a carbocation, due to the destabilising effect of the fluoroalkyl group on the resulting positive change. We have reported [3] some interesting steric and electronic effects of the bulky perfluoroalkyl group $CF_3(C_2F_5)_2C$ on the reactivity and stability of some derivatives and we now show its effect on the chemistry of the diazoalkane (3).

RESULTS

In a previous paper [3] we briefly reported the preparation of (3) from the reaction of the amine salt (1) with sodium nitrite. The salt (1) was obtained in a somewhat hazardous reaction between the acid $CF_3(C_2F_5)_2CCH_2CO_2H$ and sodium azide in oleum at 80°. Although this process gives the desired salt, it is not amenable to scale up and we have sought an improved synthesis. In our earlier study, [3] we had shown that the isocyanate $CF_3(C_2F_5)_2CCH_2NCO$ under normal Curtius-Schmidt reaction conditions afforded the urea $(CF_3(C_2F_5)_2CCH_2NH)_2CO$ which we could not hydrolyse. The isolation of this urea, however, clearly indicated the formation of amine, but that under the reaction conditions used it was reacting rapidly with the starting isocyanate. We thus reasoned that either formation of the amine, in the absence of the isocyanate, or by trapping it before it could react further should lead to a more suitable synthesis from the readily available isocyanate, thus by- passing the sodium azide route.

The first attempt was to prepare the t-butyl carbamate ester by reaction of the isocyanate with t-butanol. This reaction proceeded readily to give the desired derivative. However, as with the urea, all attempts at hydrolysis or thermolysis failed.

The second method attempted was to carry out an acid catalysed hydrolysis reaction of the isocyanate under dilute conditions with good dispersion of the isocyanate. The method we used, which proved to be successful, was the addition, via a syringe, of a solution of the isocyanate in dimethoxyethane, which takes advantage of the solubility of the latter in acids. By this method very good yields (83%) of the amine salt (1) were obtained using 98% sulphuric acid as the hydrolysing agent. Thus, we have established a good route to the amine salt (1) without using the sodium azide/oleum method.

In the course of our attempts to improve the preparation of the diazoalkane we met with two very surprising results. Firstly, in order to check whether we had prepared the amine salt (1) we wished to measure its ^{1}H and ^{19}F *n.m.r. spectra. It was found* that d^{6} *dimethyl sulphoxide was* the only solvent we could use to dissolve the salt. The ^{1}H spectrum showed no protons to be present and the ^{19}F spectrum was characteristic of the $CF_3(C_2F_5)_2C$ group. A re-run of the spectrum in ^{6}H DMSO gave a spectrum with a broad proton resonance present between 2.94 and 4.69 ppm and we were able to identify this product from this spectrum as the alkane (2) which we had prepared previously. Subsequently in a larger scale experiment (2) was isolated and fully characterised as being identical to an authentic sample.

The second suprise came in a study of the diazotisation of the salt (1) to give the diazoalkane (3). An i.r. band at 2280 cm^{-1} was observed and the intensity of this band increased with increasing concentration of sodium nitrite until with a 10M solution of the nitrite the concentration of the new product giving this i.r. band had increased to about 40% of the mixture. Addition of sodium dihydrogen phosphate considerably diminished the formation of this new product. It was possible to separate this material from the diazoalkane (3) by semi-preparative gas chromatography and to confirm that the 2280 cm^{-1} i.r. band was due entirely to this compound. Such i.r. bands are usually associated with heterocumulenes and this band compares with that due to our starting isocyanate. The ^{19}F n.m.r. spectrum showed the presence of the $CF_3(C_2F_5)_2C$ group and the proton spectrum showed the absence of any protons. Mass spectrometry gave peaks at m/z 223 and 181, corresponding to $M-C_2F_6$ and $M-C_2F_6-NCO$ for a molecule with M = 359. These data suggest the compound to be $CF_3(C_2F_5)_2$· CNCO (4). Reaction of (4) with ammonia afforded the corresponding urea (5) but all attempts to hydrolyse (4) to the amine $CF_3(C_2F_5)_2$ CNH_2 failed. This is in contrast to the ready hydrolysis of $(CF_3)_3CNCO$[4] and  [5].

This seems to be a further example of the steric effect previously observed in reactions of $CF_3(C_2F_5)_2C$ derivatives. We next studied the stability of the diazoalkane to heat and ultra- violet light. After testing small quantities of (3) to slowly increasing temperatures, with no violent reactions, and indeed little decomposition, we finally heated the neat liquid at its boiling point for ten days, when,as indicated by i.r. spectroscopy, the material had all decomposed (loss of band due to the CHN_2 group). A crystalline solid resulted which showed in its ^{19}F n.m.r. spectrum the presence of the $CF_3(C_2F_5)_2C$ group and in the ^1H spectra a single resonance at 8.15δ. Mass spectrometry indicated at m/z 692 (M^+)

and 673(M-F)$^{+}$ corresponding to $C_{14}H_2F_{26}N_2$. Thus we conclude the product to be the azadiene(7).

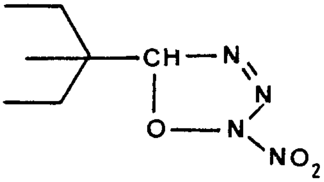
Treatment of (3) with a crystal of copper (II) perchlorate at 100° for 4hr in a sealed tube gave a mixture of two products in the ratio (8:1). These were readily identified as the azadiene (7) and the aldehyde (6), by comparison with authentic samples.

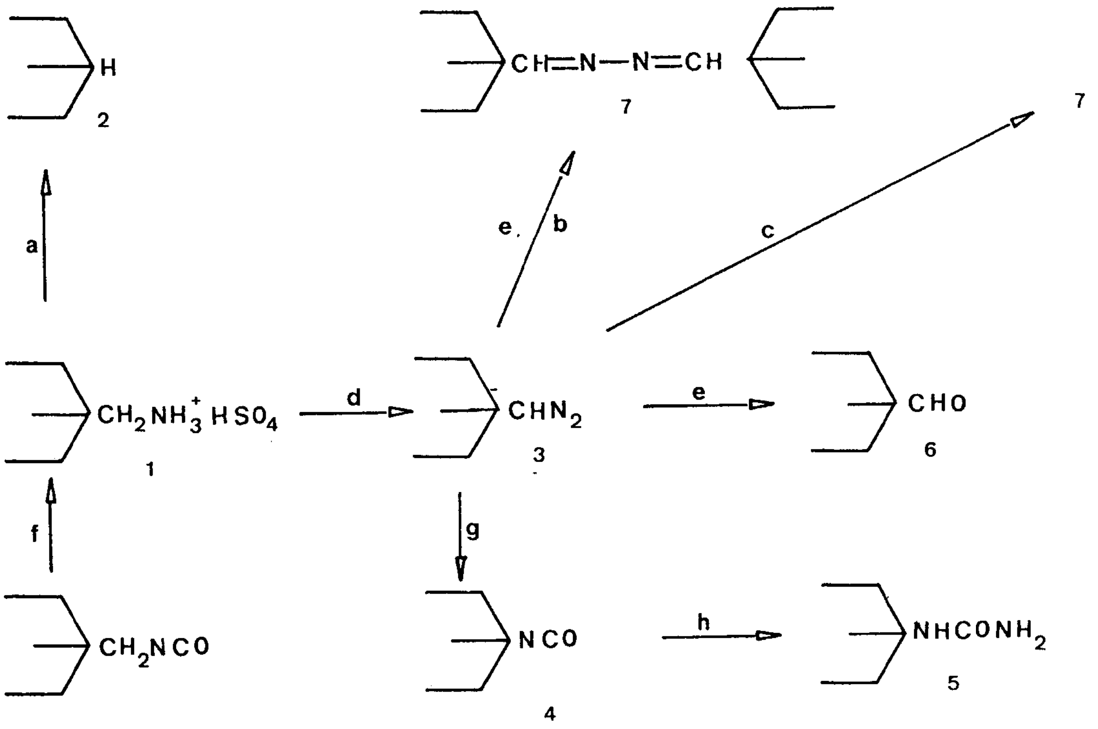
Irradiation of a sample of (3) in a sealed tube with ultra voilet light afforded after prolonged reaction (475hr) the azadiene (7).

DISCUSSION

From the above results there are clearly some unusual reactions occurring. Firstly in the ready decomposition of the amine salt with DMSO, it is believed that the reaction follows the release of some free amine from the salt. We would expect the amine to be a relatively weak base due to the presence of the fluoroalkyl groups (cf K_B $C_2H_5NH_2$, $45x10^{-4}$;K_B $CF_3CH_2NH_2$, $5x10^{-9}$). In DMSO solution the salt is likely to dissociate to some extent. Further the relative acidity of the amine protons would facilitate their removal by DMSO to give the anion $CF_3(C_2F_5)_2$ $CH_2NH^{(-)}$ which readily decomposes with loss of the $CF_3(C_2F_5)_2C^{(-)}$ anion,itselfknown to be a good leaving group[6]. The alcohol $CF_3(C_2F_5)_2CCH_2OH$ has subsequently been shown to decompose in basic solution in a similar manner[7].

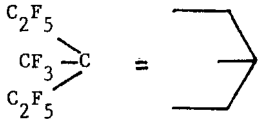
The formation of the isocyanate (4) similarly was unexpected; it is suggested that this species arises from an intermediate of the type





Reagents a; D M S O b; Δ c; h v d; $NaNO_2/H_2O$ e; C u + +

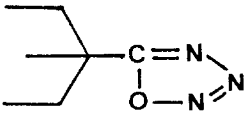
f; H^+/H_2O g.; $NaNO_2$ h; NH_3 .



SCHEME 1

This would be formed by 1,3 dipolar addition of N_2O_3 to the diazo-compound (3).

Loss of HNO_2 would then yield the heterocycle



which on loss of nitrogen would yield the nitrene $CF_3(C_2F_5)_2C\underset{\overset{\|}{O}}{C}N:$ followed by rearrangement to the isocyanate (4). The diazoalkane (3) was more stable than expected and could be stored for months in a refrigerator without decomposition. As has been indicated, prolonged heating or photolysis leads to the formation of a single component the diazadiene (7), which presumably arises by reaction of the carbene $CF_3(C_2F_5)_2$ C CH: with the diazoalkane (3). Such reactions are known for decomposition of other diazoalkanes [8] and similar mechanisms have been proposed in these cases.

The copper (II) catalysed decomposition of (3) whilst giving mostly the diazadiene (7) also gave a significant (c.a. 10%) yield of the aldehyde (6) and we attribute the formation of this latter to reactions of the carbene with oxygen, since no precautions were taken to exclude air from the reaction.

EXPERIMENTAL

3,3,4,4,4-Pentafluoro-2-pentafluoroethyl-2-trifluoromethyl butyl ammonium sulphate (1). 3,3,4,4,4-Pentafluoro-2-pentafluoroethyl-2-trifluoromethyl butyl isocyanate (10.8g 29mmol) in dimethoxyethane ($50cm^3$) was rapidly added in ten (each $5cm^3$) aliquots via a syringe, to vigorously stirred 98% sulphuric acid ($200cm^3$), when the initial exothermic reaction had ceased, the mixture was cooled and poured into iced water ($500cm^3$).

The resultant slurry was filtered off and dried in vacuo over concentrated H_2SO_4 to yield the 3,3,4,4,4-pentafluoro-2-pentafluoro ethyl-2-trifluoro methyl butyl ammonium sulphate (1) (10.6g 83%) identical to a sample prepared previously [3].

The salt (10g) was stirred in dimethyl sulphoxide (20cm^3) at 18^o for 3 hr when the mixture were carefully distilled using a 10cm vigreaux column to yield 3H-3-trifluoromethyl decafluoropentane (2) (4.3g) identical to an authentic sample[9].

4-Diazo-1,1,1,2,2-pentafluoro-3-pentafluoroethyl-3-trifluoro methylbutane(3)- Sodium nitrite (50g) in water (300cm^3)was slowly added to a vigorous stirred suspension of the salt (1) (334g) and sodium dihydrogen phosphate (450g) in water (3000cm^3) at 18^o. When the addition was complete the mixture was stirred under reflux for 2hr and then cooled. The intensely yellow lower fluorocarbon layer was separated and washed with water to give 4-diazo-2-pentafluoroethyl-3,3,4,4,4,-pentafluoro-2-trifluoromethyl butane (3) (213.9g) bp 113^O identical to a sample previously prepared [3].

3-Isocyanato-3-trifluoromethyl decafluoropentane (4) Sodium nitrite (48g) in water (40cm^3) was added to a vigorously stirred suspension of the amine salt (1)(27g) in 4M hydrochloric acid (60cm^3). The mixture was stirred at 18^o for three hours. The lower fluorocarbon layer (19.5g) was separated and shown by glc to contain two major components. Separation by preparative glc afforded (i) 3-isocyanato-3-trifluoromethyl decafluoropentane(4) nc (4.6g) bp 105^o (Found: C, 23.0; F, 68.7; N.4.2% C_7F_{13} NO requires C,23.3;F,68.4;N 3.9%) ir. 2280cm^{-1} (NCO); m/z 361(M$^+$), 342 (M-F), 292 (M-CF_3); ^{19}F nmr. was consistent with the presence of the $CF_3(C_2F_5)_2C$ group: and (ii) the diazo-compound (3) (7.3g).

Dry ammonia was bubbled into a solution of the isocyanate (4) (0.5g) in dry ether for 2 hr. The solvent was evaporated to give *N-perfluoro (3-methylpent-3-yl) urea* (5) nc (0.3g) m p 65^{0} (Found: C, 22.1, H, 0.9 F, 63.7% $C_7H_3F_{13}N_2O$ requires C,22.2; H,0.8, F.65.5%); i.r. 3120-3550cm^{-1} (broad band NH) 1675 and 1600cm^{-1}(CONH$_2$);^{1}H n.m.r. a broad band 5.02-6.25 which disappeared on addition of D_2O; m/z 378 (M^+), 359 (M-F)

Decomposition of the Diazobutane (3)

(a) *Heating alone* - The diazoalkane (3) (3.6g) was heated under reflux for 10 days. The intense yellow colour of the diazoalkane changed slowly to a pale orange, on cooling the mixture solidified. The solid was filtered off and purified by sublimation to yield *1,1,1,2,2,9,9,10,10,10-decafluoro-3,7-bis (pentafluoroethyl)-3,7-bis (trifluoromethyl)-5,6-diaza-deca-4,6-diene*(7) nc (1.6g) mp 44° (Found: C,24.3; H,0,4; F,71.2; N,4.5%. $C_{14}H_2F_{26}N_{26}N_2$ requires C,24.3; H,0.3 F, 71.4, N, 4.1%)

(b) *With Cu^{II}perchlorate* - The diazoalkane (3) (5.0g) and a crystal of copper (II) perchlorate (0.01g) were sealed in a Carius tube and heated at 100° for 4 hr when the yellow colour had disappeared. Gas chromatography showed the product to be a mixture of two components, in the ratio (8:1). Separation of a portion of the product (2g) by semi-preparative glc gave (i) the aldehyde (6) (0.3g) identical to an authentic sample [7] and (ii) the diazadiene (7) (1.3g) identical to an authentic sample.

(c) *By irradiation* - The diazobutane (3) (3.3g) sealed in a Carius tube was irradiated with a medium pressure mercury lamp for 475hr. The colour disappeared and a solid mass was formed when the tube cooled. Filtration from the small amount of residual liquid and sublimation afforded the diazadiene (7)) (1.06g).

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