FLUORINE-CONTAINING HETEROCUMULENES

18*. FLUORIDE-CATALYZED REACTIONS OF HEXAFLUOROACETONE AND PERFLUOROISOBUTYLENE WITH SULFINYLAMINES

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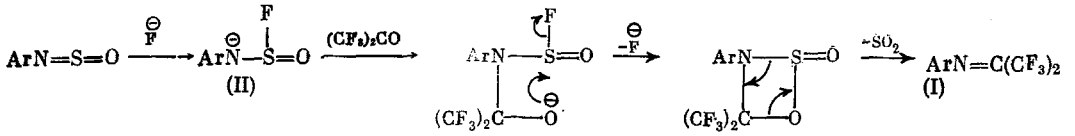
In continuation of our research [2] into the reactions of heterocumulenes with compounds containing electrophilic short bonds, we have investigated the reaction of hexafluoroacetone (HFA) and perfluoroisobutylene (PFIB) with sulfinylamines under conditions of nucleophilic catalysis.

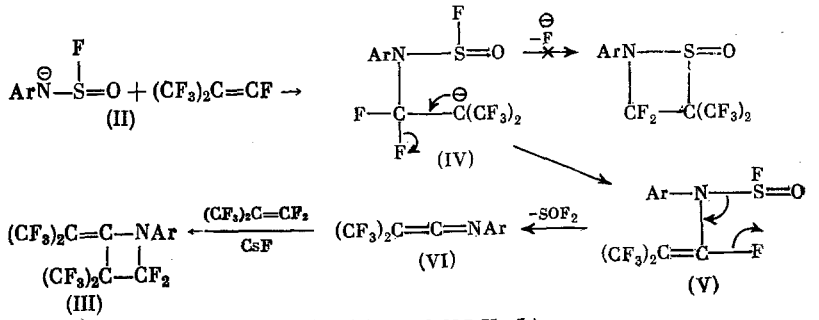
Unlike unfluorinated carbonyl compounds [3], HFA does not react with sulfinylaniline even when heated (100°C) for long periods. In the presence of CsF in CH_3CN, however, this reaction goes readily at 0-20°C and gives the anil (Ia) of HFA in high yields. The p-nitro derivative (Ib) was prepared analogously



Ar=C_6H_5 (a), p-$O_2NC_6H_4$ (b)

The role of the catalyst in this reaction evidently consists in converting the electrophilic sulfinylamine into a nucleophilic anion (II), which is capable of adding on to the carbonyl group in HFA. The end products of the reaction are formed by cyclization (with regeneration of the catalyst) and decomposition of the cycloadduct. The reaction of perfluoro ketones with isocyanates, which results in the formation of perfluoro ketone imines when catalyzed by alkali metal fluorides, evidently goes according to the same reaction scheme [4,5].

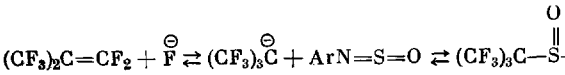
Attempts to react PFIB with isocyanates in the presence of CsF proved unsuccessful. Thus, reaction of PFIB with PhN=C=O and CsF resulted only in dimerization of the isocyanate. At the same time, perfluoropropyl isocyanate reacts with CsF or Et_3N to form stable adducts



Ar = C_6H_5 (a), p-$O_2NC_6H_4$ (b)

*See [1] for communication 17.

†The PFIB–CsF system is a source of the anion $(CF_3)_3C^-$ [8], which could act like a Grignard reagent [9] and add on to the sulfinylamines to form perfluoro-t-butylsulfinamides. Such products are not detected, however, possibly due to the reversibility of the addition of the $(CF_3)_3C^-$ anion to the heterocumulene



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[6,7] which do not react with PFIB (after prolonged contact at 20°C in CH_3CN). Sulfinylamines react with PFIB in the presence of CsF (the reaction does not go in the absence of a catalyst) to form ultimately azetidines (III).† In this case, the intermediate carbanion (IV) is evidently stabilized not by cyclization but by elimination of a vinylic fluorine atom (cf. [10]). The vinylic substitution products (V) are then converted to ketenimines (VI), which add yet another molecule of PFIB under the influence of CsF [2]

This reaction scheme is confirmed by the fact that reaction of PFIB with N-sulfinylbenzenesulfonamide (VII) gives an adduct (VIII) of N-benzenesulfonyl-bis(trifluoromethyl)-ketenimine with CsF. The reaction stops at this stage because (VIII) is not capable of reacting with PFIB [2]

$$(CF_3)_2C{=}CF_2 + C_6H_5SO_2N{=}S{=}O \xrightarrow[CsF]{-SOF_2} (CF_3)_2C{=}C{=}NSO_2C_6H_5 \cdot CsF$$

(VII) (VIII)

EXPERIMENTAL

Reaction of Hexafluoroacetone with Sulfinylamines. A suspension of 1.5 g of freshly calcined CsF, 3.9 g PhNSO, and 30 ml of abs. CH_3CN was treated gradually with 6 g of HFA while stirring and cooling with ice. The mixture was warmed to 20°C, part of the solvent was distilled off, and the residue was poured into dilute HCl (1:5). The resulting oil was extracted with ether, dried over $MgSO_4$, and distilled to give 6.3 g (88%) of anil (Ia), bp 137-138°C, which was identical (GLC, ^{19}F NMR) with an authentic sample [11]. Anil (Ib) was prepared similarly; yield 79%; bp 81-85°C/2 mm; mp 34-36°C [12].

Reaction of Perfluoroisobutylene with Sulfinylamines. A suspension of 7 g CsF in 40 ml abs. monoglyme was treated with 20 g PFIB while stirring and cooling with ice, and then treated dropwise with 5.5 g PhNSO in 10 ml monoglyme. The mixture was warmed to 20°C and, after 2 h, distilled in vacuo to remove volatiles. The residue was poured into water, and the resulting oil was extracted with ether, washed with water, dried over $MgSO_4$, and distilled to give 15.3 g (85%) of azetidine (IIa), bp 75-78°C/8 mm, which was identical (GLC, ^{19}F NMR) to an authentic sample [2]. Analogously, 4 g of p-$O_2NC_6H_4NSO$ in 10 ml abs. CH_3CN, was added to 1 g CsF and 20 g PFIB in 20 ml CH_3CN, volatiles removed, and the reaction mixture worked up with water to give azetidine (IIIb) in 98% yield, mp 71-74°C (no depression with authentic sample [2]).

Reaction of Perfluoroisobutylene with N-Sulfinylbenzenesulfonamide. A suspension of 4.6 g CsF in 15 ml abs. monoglyme was cooled while adding 7 g PFIB, after which a solution of 6.1 g (VII) in 10 ml monoglyme was added dropwise. The mixture was stirred at 20°C for 12 h, volatiles removed under vacuum, and the solid residue suspended in 50 ml dry CH_2Cl_2. The suspension was saturated with dry HCl and the precipitate filtered off. The filtrate was distilled to give 4.5 g (42%) of $(CF_3)_2CHCF{=}NSO_2C_6H_5$, bp 104-108°C/3 mm, which was identical (^{19}F NMR) to an authentic sample [13].

Reaction of Perfluoroisobutylene with Perfluoropropyl Isocyanate. A suspension of 4.2 g CsF in 40 ml abs. monoglyme was stirred while adding 6 g C_3F_7NCO, after which 5.6 g PFIB was added over 1 h at 20°C. After 26 h, the unreacted PFIB was distilled off and the residue treated with 5 ml alcohol. The precipitate was filtered off and the filtrate distilled to give 1.4 g (27%) of $C_2F_5C(OEt){=}NCOOEt$, bp 69-70°C/7 mm. Found: C 36.28; H. 3.79; F 36.33%. $C_8H_{10}F_5O_3N$. Calculated: C 36.50; H 3.80; F 36.12%. IR spectrum (ν, cm^{-1}): 1720, 1745 (C=N, C=O). PMR spectrum (in CCl_4, δ, ppm): 1.2 and 1.33 t (CH_3), 4.22 and 4.35 q $(CH_2)_2$, $J_{CH_3-CH_2}$ = 7.35 Hz. ^{19}F NMR spectrum: +4.45 s (CF_3), +39.2 s (CF_2).

CONCLUSIONS

1. The CsF-catalyzed reaction of hexafluoroacetone with sulfinylamines is a convenient method for synthesizing hexafluoroacetone imines.

2. Reaction of perfluoroisobutylene with sulfinylamines in the presence of CsF gives adducts of bis(trifluoromethyl)ketenimines with perfluoroisobutylene.

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CYANOACETYLENE AND ITS DERIVATIVES.

2. REACTION OF ISOMERIC CYANOMETHYLACETYLENE–CYANOALLENE WITH GLYCOLS

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Acetylenes activated by an α-nitrile group are highly reactive with nucleophilic reagents [1]. Cyanomethylacetylene also reacts readily with nucleophiles to form products corresponding to addition to the isomeric allene [2], indicating the facility with which acetylene–allene isomerization takes place among the cyanomethylacetylenes. This type of reaction of substituted acetylenes was discovered and studied in detail by Favorskii [3].

In order to determine the conditions under which cyanomethylacetylene (Ia) and its isomer cyanoallene (Ib) react with bifunctional nucleophiles and the direction which the reaction takes, we have studied the addition of glycols to this isomer pair, with a cyanoallene content of up to 45%. We found that ethylene glycol reacts with nitriles (Ia,b) in the presence of catalytic amounts of MeONa to form 2-methyl-2-cyanomethyl-1,3-dioxolane (III) in yields of up to 70%. The reaction evidently proceeds in two steps. An ethylene glycol monoether (II) is first formed, and this then undergoes intramolecular cyclization to form the dioxolane (III). We did not succeed in isolating the intermediate product, however, evidently due to the high rate of formation of five-membered rings. Severe heating of the reaction mixture occurs during the reaction of ethylene glycol with (Ia,b), so the nitrile should be added slowly, since a rapid increase in temperature would cause severe resin formation (see scheme).

The stepwise nature of the reaction is clearly confirmed in the case of the reaction of (Ia,b) with 1,3-glycols (1,3-propylene glycol). The propylene glycol monoether, i.e., 1-methyl-1-(3-hydroxypropoxy)-2-cyanoethane (IV), the cyclic acetal (V), and the corresponding diether (VI) can be isolated from the reaction mixture and characterized. Under analogous conditions, 1,4-butanediol forms only linear products. It should be noted that in studying the reactivity of substituted cyanoacetylenes with 1,3-glycols we were able to isolate only cyclic acetals. The structure of the synthesized compounds was confirmed by IR and PMR spectroscopy, and their composition was confirmed by elementary analysis.

The IR spectra of cyclic acetals (III), (V), and (VIII) contain absorption bands at ν = 2260-2270 cm^{-1} (CN) and 1050-1160 cm^{-1} (COC) and contain no absorption bands corresponding

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