Poly(bistrifluoromethylamino)-compounds. Synthesis of *NN*-Bistrifluoromethylamino-substituted Allenes and their Reaction with Trifluoronitrosomethane

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Summary A series of novel *NN*-bistrifluoromethylamino-substituted allenes has been synthesised; trifluoronitrosomethane converts them into the corresponding oxazetidines which on pyrolysis afford *NN*-bistrifluoromethylformamide and an *N*-trifluoromethylketenimine.

IT is increasingly apparent that a family of stable poly(bistrifluoromethylamino)-compounds can be obtained in which the $(CF_3)_2N$ group has replaced hydrogen in organic compounds in much the same way as the perfluorocarbons may be regarded as derived from hydrocarbons by replacement of hydrogen by fluorine. *NN*-Bistrifluoromethylamino-substituted olefins[1-3], acetylenes[3,4] and butadienes[5] have recently been prepared, and a useful route to $(CF_3)_2N$-substituted allenes of type $(CF_3)_2N{\cdot}CR^1{:}C{:}CR^2R^3$ [(I), $R^1 = R^2 = R^3 = H$; (II), $R^1 = (CF_3)_2N, R^2 = R^3 = H$; (III), $R^2 = (CF_3)_2N$, $R^1 = R^3 = H$; (IV), $R^1 = R^2 = (CF_3)_2N$, $R^3 = H$] has now been found by the dehydrobromination of the adducts formed by the reaction of *N*-bromobistrifluoromethylamine with allenes (Table).

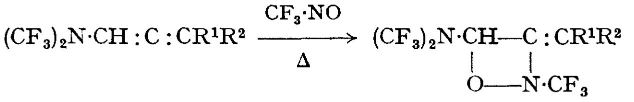
The vapour-phase reactions of the *N*-bromo-amine with allene in daylight are considered to proceed *via* free-radical intermediates,[6] while the liquid phase reactions at −78° in the dark probably proceed *via* ionic intermediates.[2,7] The $(CF_3)_2N$-substituted allene (II) did not react with the *N*-bromo-amine either under comparable free-radical or ionic conditions. Reaction of the allene (IV) with the *N*-bromo-amine did not give the expected adduct $[(CF_3)_2N]_2$-$CH{\cdot}CBr{:}C[N(CF_3)_2]_2$, but yielded the brominated allene (V) and *NN*-bistrifluoromethylamine; electrophilic attack of Br+ from NBr with loss of H+ is indicated.

Allene*	Products	Dehydrobromination products $(CF_3)N_2{\cdot}CR^1{:}C{:}CR^2R^3$
$CH_2{:}C{:}CH_2$†	$(CF_3)_2N{\cdot}CH_2{\cdot}CBr{:}CH_2$ (85%)	(I) (93%) and
	$(CF_3)_2N{\cdot}C(CH_2Br){:}CH_2$ (10%)	$(CF_3)_2N{\cdot}CH_2{\cdot}C{\vdots}CH$ (5%)
$CH_2{:}C{:}CH_2$†‡	$(CF_3)_2N{\cdot}CH_2{\cdot}CBr_2{\cdot}CH_2{\cdot}N(CF_3)_2$ (97%)	(III) (97%)
$(CF_3)_2N{\cdot}CH{:}C{:}CH_2$	$[(CF_3)_2N]_2CH{\cdot}CBr{:}CH_2$ (71%)	(II) (96%)
	$(CF_3)_2N{\cdot}CH_2{\cdot}CBr{:}CH{\cdot}N(CF_3)_2$ (24%)	
$[(CF_3)_2N]_2C{:}C{:}CH_2$	No reaction	
$(CF_3)_2N{\cdot}CH{:}C{:}CH{\cdot}N(CF_3)_2$	$[(CF_3)_2N]_2CH{\cdot}CBr{:}CH{\cdot}N(CF_3)_2$ (98%)	(IV) (98%)
$[(CF_3)_2N]_2C{:}C{:}CH{\cdot}N(CF_3)_2$	$[(CF_3)_2N]_2C{:}C{:}CBr{\cdot}N(CF_3)_2$ (V) (93%)	
	$(CF_3)_2NH$ (98%)	

* 1:1 Molar ratio of reactants in the liquid phase at −78° in the dark unless otherwise stated.
† Vapour phase at *ca.* 20° in daylight. ‡ 2:1 Molar ratio of $(CF_3)_2NBr$: allene.

Dehydrobromination of the products by potassium hydroxide proceeded smoothly to give the allenes shown (Table) and in only one case was an isomeric acetylene observed.

On thermal reaction with trifluoronitrosomethane the allenes (I), (III), and (IV) gave the corresponding cyclic oxazetidines (VI) [(VIa); $R^1 = R^2 = H$, 47%: (VIb); $R^1 = H$, $R^2 = (CF_3)_2N$, 89%: (VIc); $R^1 = R^2 = (CF_3)_2N$, 32%]; allene (II) did not react under comparable conditions.


(VI)

The oxazetidine structures were established by flow pyrolysis (200—300°) which gave equimolar quantities of *NN*-bistrifluoromethylformamide and the corresponding *N*-trifluoromethylketenimine (VII) [(VIIa); $R^1 = R^2 = H$, 100%: (VIIb); $R^1 = H$, $R^2 = (CF_3)_2N$, 98%: (VIIc); $R^1 = R^2 = (CF_3)_2N$, >90%] by ring cleavage.

$$\text{(VI)} \xrightarrow{\Delta} (CF_3)_2N\cdot CHO + \underset{\text{(VII)}}{CF_3\cdot N{:}C{:}CR^1R^2}$$

All of the new compounds had satisfactory elemental analyses and their structures were established by n.m.r. and mass spectroscopy.

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