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PRELIMINARY NOTE

Reaction of Bistrifluoromethylaminosulphenyl Chloride with Hydrocarbon Olefins and the Synthesis of Bistrifluoromethylaminosulphenylarenes

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SUMMARY

Reaction of bistrifluoromethylaminosulphenyl chloride with acyclic and alicyclic hydrocarbon olefins at -78 °C in the dark affords 1:1 adducts of type $(CF_3)_2NS\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}Cl$ in high yield. Treatment of diaryl disulphides with the N-bromo-amine $(CF_3)_2NBr$ or of benzenesulphenyl chloride with the mercurial $[(CF_3)_2N]_2Hg$ provide convenient routes to bistrifluoromethylaminosulphenylarenes.

The only organic compounds reported to date containing the $(CF_3)_2NS$ group, apart from the sulphides $[(CF_3)_2N]_2S$(I) and $[(CF_3)_2N]_2S_2$ (II) [1], are the sulphenyl chloride $(CF_3)_2NSCl$ (III) {from $(CF_3)_2NCl$ + S or $(CF_3)_2NH$ + SCl_2 under thermal conditions [2] and $[(CF_3)_2N]_2Hg$ + SCl_2 at 20 °C or $(CF_3)_2NCl$ + S_2Cl_2 + u.v. [3]} and the alkanes $(CF_3)_2NSMe$ (IV) {from MeSCl + $[(CF_3)_2N]_2Hg$ at 20 °C [4]} and $(CF_3)_2NSCF_3$ {from CF_3SCl + $[(CF_3)_2N]_2Hg$ at 80 °C or CF_3SSCF_3 + $(CF_3)_2NCl$ + u.v. [4]}, although previous work

TABLE

Reaction of the sulphenyl chloride (III) with hydrocarbon alkenes

Alkene (g, mmole)	(III) (g, mmole)	Alkene recovered (%)	Products (% yield)
$CH_2=CMe_2$ (1.65, 29.4)	(3.33, 15.17)	48.5	$(CF_3)_2NSCH_2CMe_2Cl$ 81, (VI) + (VII) 6.5
$CH_2=CHEt$ (0.72, 12.86)	(1.00, 4.56)	60	$(CF_3)_2NSCH_2CHEtCl$ $(CF_3)_2NSCHEtCH_2Cl$ } 94*
$CH_2=CHPr^n$ (0.45, 6.43)	(1.08, 4.92)	37.5	$(CF_3)_2NSCH_2CHPr^nCl$ $(CF_3)_2NSCHPr^nCH_2Cl$ } 82.5*
$CH_2=CHCMe_3$ (1.02, 12.11)	(2.77, 12.82)	6.5	$(CF_3)_2NSCH_2CHClCMe_3$ 82
$MeCH=CMe_2$ (0.53, 7.57)	(1.69, 7.70)	9.5	$(CF_3)_2NSCHMeCMe_2Cl$ 88

Table continued.....

cis-MeCH=CHMe (0.64, 11.43)	(1.24, 5.65)	43.5	threo-$(CF_3)_2NSCHMeCHMeCl$ 89
trans-MeCH=CHMe (0.49, 8.75)	(0.83, 3.78)	57	erythro-$(CF_3)_2NSCHMeCHMeCl$ 92
cyclopentene (0.51, 7.50)	(1.56, 7.11)	14	trans-$(CF_3)_2NSCH(CH_2)_3CHCl$ 89
cyclohexene (0.91, 11.10)	(0.98, 4.46)	66	trans-$(CF_3)_2NSCH(CH_2)_4CHCl$ 82

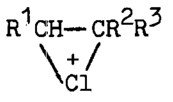
All reactions were carried out *in vacuo* in sealed tubes at -78 °C in the dark (5 to 7d) and also gave $(CF_3)_2NH$ (1 to 11.5%). *The adduct mixtures could not be separated by g.l.c.

$(CF_3)_2NSCH_2CHMe=CH_2$

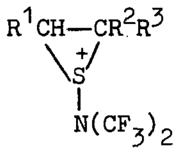
(VI)

$(CF_3)_2NSCH=CMe_2$

(VII)



(VIII)



(IX)

in this department [5] has shown that the N-bromo-amine $(CF_3)_2NBr$ undergoes reaction with the disulphides MeSSMe and PhSSPh at 20 °C in daylight to give the compounds (IV) and $(CF_3)_2NSPh$, respectively.

The reaction of the sulphenyl chloride (III) with ethylene at 70 °C has been investigated and gave the compounds (I), $(CF_3)_2NH$, $CF_3N{=}CF_2$, SiF_4 and $(ClCH_2CH_2)_2S$ [4]. These products, together with those obtained from the reactions with silver difluoride and silver cyanide [4], were stated as indicating that the sulphenyl chloride (III) tends to behave as a mixture of the sulphide (I) and sulphur dichloride.

In the present work the sulphenyl chloride (III) was prepared by treatment of the mercurial $[(CF_3)_2N]_2Hg$ with sulphur dichloride [3] and its reaction with various hydrocarbon olefins was investigated; the results obtained are summarised in the Table.

The additions are trans-stereospecific and could involve cyclic chloronium (VIII) or sulphonium (IX) ions as intermediates. The detection of the $(CF_3)_2NS$-substituted alkenes (VI) and (VII) in the products from the 2-methylpropene reaction could be cited as evidence in favour of the latter intermediates (IX) and the observation that the chlorine atom in the major (or exclusive) 1:1 adduct is bonded to the carbon atom most able to stabilise a positive charge is consistent with this. However, it is difficult to explain monodirectional addition to the olefin $CH_2{=}CHBu^t$ but bidirectional addition to the less bulky olefins $CH_2{=}CHR$ (R=Et or Pr^n) on the basis of intermediates of type (IX). It is therefore more probable that cyclic chloronium ion intermediates (VIII) are involved and that the alkenes (VI) and (VII) arise by dehydrochlorination of the 1:1 adduct $(CF_3)_2NSCH_2CMe_2Cl$. In this context it has been found previously that treatment of the olefin $CH_2{=}CHBu^t$ with bromine in methanol gave dibromide and the ether $MeOCH_2CHBrBu^t$ while similar treatment of the olefin $CH_2{=}CHBu^n$ gave dibromide and the ethers $MeOCH_2CHBrBu^n$ and $MeOCHBu^nCH_2Br$ (ratio 1:4)[6].

The bistrifluoromethylaminosulphenylarenes $XC_6H_4SN(CF_3)_2$ (X) [X=H (30%), X=4-Cl (77%), X=4-Br (69%)] were obtained by treatment of the appropriate diaryl disulphide with N-bromobistrifluoromethylamine at 20 °C in daylight (24h) while the reaction of mercuric bistrifluoromethylamide with benzenesulphenyl chloride under comparable conditions gave the compounds (X) where X=H (76%) and X=4-Cl (4%).

The reaction of the sulphenyl chloride (III) with anisole (20 °C, dark, 48h) afforded the compounds $(CF_3)_2NH$ (68%), HCl (66%), (I) (21%) and the sulphide $[4\text{-}MeOC_6H_4]_2S$ (41%) while reaction with phenol (20 °C, dark, 24h) in ether as solvent gave (I) (95%) and 4-chlorophenol (97%).

The isolated 1:1 adducts (or mixtures of 1:1 adducts as indicated in the Table) and the arene derivatives (X) possessed correct elemental compositions and their structures were established spectroscopically [i.r., n.m.r. (^1H and ^{19}F) and mass].

1 J.A. Young, S.N. Tsoukalas, and R.D. Dresdner, J.Amer. Chem.Soc., 82 (1960) 396.

2 C.W. Tullock, U.S.P., (1964) 3121112.

3 H.J. Emeléus and B.W. Tattershall, J.Chem.Soc., (1964) 5892.

4 H.J. Emeleus and B.W. Tattershall, J.Inorg.Nuc.Chem., 28 (1966) 1823.

5 B. Haley, Ph.D. Thesis, Manchester (1974).

6 W.H. Puterbaugh and M.S. Newman, J.Amer.Chem.Soc., 79 (1957) 3469.