Journal of Fluorine Chemistry, 34 (1986) 201–207

Received: October 28, 1985; accepted June 11, 1986

SYNTHESES WITH UNSATURATED NITRILES. PART VII. TRIFLUOROMETHANESULFENYLATION OF YLIDENEMALONONITRILE DIMERS.

MARIA J. MOKROSZ

Department of Organic Chemistry, Jagiellonian University,
Karasia 3, 30-060 Cracow (Poland)

SUMMARY

The alkylidenemalononitrile dimers 1-4 reacted smoothly with trifluoromethanesulfenyl chloride to yield 1-amino-2,2,6-tricyano-3,3-alkyl-5[(trifluoromethylthio)alkyl] -1,3-cyclohexadienes 5-7 and 9. IR, UV and ^{1}H NMR spectra of the obtained products have been presented.

INTRODUCTION

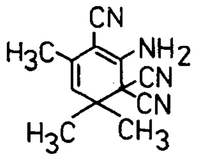
The alkylidenemalononitrile dimers undergo nucleophilic addition very easily as was shown before [1,2]. The presence of the allylic or vinyl hydrogen atoms, however, makes them also susceptible towards electrophilic substitution. The reaction with bromine [3] showed that the alkylidenemalononitrile dimers behave as C-H acids and are converted into mono-, di- and trisubstituted products, but the substitution multiplicity depends on the particular dimer. Continuing the study on the reactivity of these dimers the trifluoromethanesulfenylation reaction has been undertaken.

RESULTS AND DISCUSSION

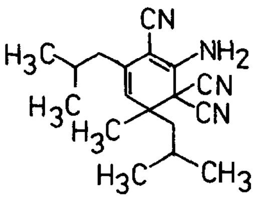
The reactions have been carried out in a vacuum vessel in $CHCl_3$ at room temperature. Under these conditions the alkyli-

0022-1139/86/$3.50

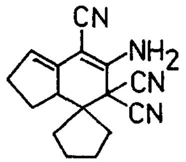
denemalononitrile dimers 1-4 reacted with an excess of trifluoromethanesulfenyl chloride easily.



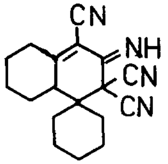
1



2



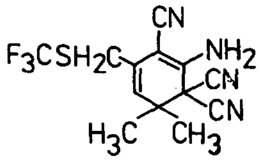
3



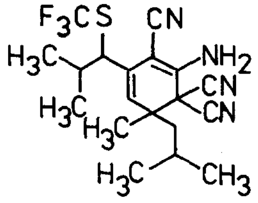
4

Contrary to the bromination reaction, sulfenylation of compounds 1-4 led to the monosubstituted products 5-9 (n.c.) exclusively, except dimer 1 which formed also a small amount of the di-substituted compound 10 (5%) (n.c.).
The obtained compounds were characterized by IR, ^{1}H NMR and UV spectra. IR spectra of the compounds 5-7, 9 and 10 showed NH$_2$ stretching vibrations in the range 3200-3400 cm^{-1} and deformation vibration bands in the 1550-1590 cm^{-1} range. CN and C=C stretches appeared about 2200 cm^{-1} and at 1640-1660 cm^{-1}, respectively. One can also abserved the strong absoption for SCF$_3$ group in the 1100-1160 cm^{-1} range.
The ^{1}H NMR spectrum of compound 5 showed four singlets, at 1.45 ppm due to two methyl groups, at 2.75 ppm for the CF$_3$S-substituted methylene group, at 5.67 for the amino and at 6.37 for the vinyl protons. The di-substituted product 10 showed also a singlet at 1.46 ppm for two methyl groups, a singlet

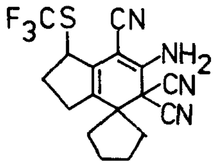
for the substituted methylene group at 3.28 ppm and a downfield shifted broad singlet for NH_2 protons at 7.2 ppm. In ^{19}F NMR spectra, one signal at 43.6 ppm and two signals at 43.93 and 44.14 ppm were observed for 5 and 10, respectively.



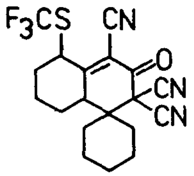
5



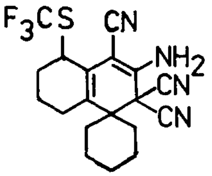
6



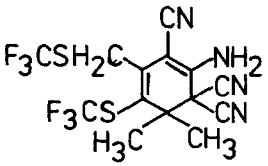
7



8



9



10

The ^1H NMR spectrum of 6 revealed a multiplet at 1.03 ppm for four methyl groups, a singlet at 1.43, a quartet at 1.52 and a doublet at 1.77 ppm for $-CH_3$, $\mathrm{C\underline{H}(CH_3)_2}$ and methylene groups, respectively. A doublet at 3.67 and a quartet at 2.17 ppm corresponded to methine protons α- and β- to the CF_3S group, respectively. The vinyl proton appeared at 5.55 ppm and the NH_2 group at 5.78 ppm.

A broad multiplet in the 1.4-2.3 ppm range in the ^1H NMR spectrum of spirocompound 7 corresponded to ten protons, i.e. eight of spiro and two of fused cyclopentane rings. Two doublets of J=9 Hz at 3.3 and 2.75 ppm indicated the CF_3S-substituted methine group and adjacent methylene protons. NH_2 protons were observed as a broad singlet at 5.6 ppm.

Sulfenylation of dimer 4 afforded two monosubstituted products and the predominant one was identified as the amino compound 9. The ^1H NMR spectrum consisted of a broad multiplet at 1.1-2.5 ppm for 16 protons of the cyclohexane rings, a singlet at 4.25 for one proton next to the CF_3S group and a broad singlet for the NH_2 group at 5.47 ppm. The second product appeared to be the ketone 8 which seems to form due to the presence of moisture during the reaction or work-up of the reaction mixture, as the structure of dimer 4 facilitates its hydrolysis [3,4]. The IR spectrum of 8 showed strong absorption band at 1710 cm^{-1} for the C=O group, at 1600 cm^{-1} and 2220 cm^{-1} for C=C and CN stretches, respectively, and at 1100-1160 cm^{-1} for the CF_3S group. The deshielding effect of a carbonyl group was observed in the ^1H NMR spectrum; the $C\underline{H}SCF_3$ proton was shifted down to 5.0 ppm compared to 4.25 ppm in compound 9.

A methine proton between fused cyclohexane rings appeared at 3.7 ppm and the other 16 protons were represented by a broad multiplet at 1.1-2.5 ppm.

The compounds 5-7 and 9, possessing cyclohexadiene-1,3 rings, showed two absorption bands at 210-220 nm and in the 310-330 nm range due to $n\rightarrow\pi$ and $\pi\rightarrow\pi^*$ electron transitions. The substitution of the second CF_3S group to the cyclohexadiene moiety (compound 10) did not influence the short-wavelength band but affected the $\pi\rightarrow\pi^*$ transition; thus the corresponding band showed a strong bathochromic shift (λ_{max}=362.3 nm). Ketone 8 showed only one absorption band at λ_{max}=252.5 nm typical for the carbonyl chromophore.

Compared to the bromination reaction, trifluoromethanesulfenylation of the ylidenemalononitrile dimers appeared to be much more selective. Moreover, CF_3S-substitution seems to favour the cyclohexadiene structure of the products, as the sulfenylation of dimers 3 and 4 was accompanied by a double bond migration.

The attempted trifluoromethanesulfenylation of the arylidenemalononitrile dimers and alkylidene- or arylidenemalononitrile under the above conditions has failed.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H and ^{19}F NMR spectra were obtained on a Bruker WM 250 spectrometer with TMS and hexafluorobenzene respectively, as the internal standards. IR spectra were taken on a Specord IR 75 spectrometer in nujol suspension. UV spectra were recorded on a Specord UV-VIS (Zeiss, Jena) in ethanolic solution.

General procedure for trifluoromethanesulfenylation of 1-4

In a vacuum tube 5 mM of the appriopriate dimer dissolved in 10 cm^3 $CHCl_3$ were cooled down in liquid nitrogen and an excess of CF_3SCl was condensed in under reduced pressure. The reaction mixture was stirred then at RT for 18h.

Sulfenylation of 1

The reaction mixture was evaporated to dryness and 10 cm^3 CCl_4 was added. The precipitate was filtered off and recrystallized with ethanol to give 0.2g (5%) of 10. White needles, M.p. 208-210°. IR: 3360, 3310, 3220 (NH_2), 2210 (CN), 1660 (C=C), 1550 (NH_2), 1160, 1140, 1100 (CF_3S); ^{1}H NMR ($CDCl_3$+ CF_3COOH) 1.46 (s,6H,CH_3x2); 3.28 (s,2H,CH_2SCF_3); 7.2 (bs,2H, NH_2); ^{19}F NMR 43.93, 44.14; UV λ_{max} 362.3 nm ε_{max} 32600, λ_{max} 210.5 nm ε_{max} 14000. Analysis: Found: C, 40.8; H, 2.5; N, 13.70; S, 15.20%. $C_{14}H_{10}N_4S_2F_6$ requires C, 40.78; H, 2.44; N, 13.59; S, 15.52%.

The mother liquid was chromatographed on SiO_2 with $CHCl_3$ as a mobile phase. The oily substance treated with CCl_4 crystallized to give white needles of 5 (64%) M.p. 122-123°. IR: 3380, 3300, 3200 (NH_2), 2210 (CN), 1650 (C=C), 1580 (NH_2), 1130, 1115, 1105 (CF_3S); ^{1}H NMR ($CDCl_3$) 1.45 (s,6H,CH_3x2); 2.75 (s,2H,CH_2SCF_3); 5.67 (s,2H,NH_2); 6.37 (s,1H,CH=); ^{19}F NMR 43.6; UV λ_{max} 312.5 nm ε_{max} 18600, λ_{max} 210.5 nm ε_{max} 14100. Analysis: Found: C, 49.9; H, 3.6; N, 17.8; S, 10.3%. $C_{13}H_{11}N_4SF_3$ requires C, 50.00; H, 3.55; N, 17.96; S, 10.27%.

Sulfenylation of 2

Evaporation of the reaction mixture left the oily residue which treated with CCl_4 crystallized giving white needles of 6. The mother liquid after chromatography on SiO_2 with $CHCl_3$ gave an additional amount of the same compound. M.p. 164-165°, yield 76%. IR: 3360, 3320, 3230, 3190 (NH_2), 2200 (CN), 1660 (C=C), 1570 (NH_2), 1150, 1110, 1100 (CF_3S); ^1H NMR ($CDCl_3$) 1.03 (m,12H,CH_3x4); 1.43 (s,3H,CH_3); 1.52 (q,J=7Hz,1H,$C\underline{H}(CH_3)_2$); 1.77 (d,2H,$-CH_2-$); 2.17 (q,J=9Hz,1H,$C\underline{H}CHSCF_3$); 2.67 (d,J=9Hz, 1H,$CHSCF_3$); 5.55 (s,1H,CH=); 5.78 (bs,2H,NH_2); ^{19}F NMR 41.4; UV λ_{max} 333.3 nm ε_{max} 4800, λ_{max} 217.4 nm ε_{max} 13500. Analysis: Found: C, 57.5; H, 6.2; N, 14.0; S, 8.2%. $C_{19}H_{23}N_4SF_3$ requires C, 57.56; H, 5.85; N, 14.13; S, 8.09%.

Sulfenylation of 3

The reaction mixture was worked-up as above to give 7 in 81% yield. M.p. 169-171°. IR: 3400, 3290, 3200 (NH_2), 2205 (CN), 1640 (C=C), 1595 (NH_2), 1150, 1110, 1100 (CF_3S); ^1H NMR ($CDCl_3$) 1.4-2.3 (m,10H); 2.75 (d,J=9Hz,2H,$C\underline{H}_2CHSCF_3$); 3.3 (t,J=9Hz,1H,$CHSCF_3$); 5.6 (bs,2H,NH_2); ^{19}F NMR 40.57; UV λ_{max} 317.5 nm ε_{max} 15800, λ_{max} 208.3 nm ε_{max} 14500. Analysis: Found: C, 56.2; H, 4.0; N, 15.6; S, 9.1%. $C_{17}H_{15}N_4SF_3$ requires C, 56.04; H, 4.15; N, 15.38; S, 8.80%.

Sulfenylation of 4

The dry reaction mixture was treated with CCl_4 and the precipitate of 9 was filtered off. The mother liquid was then chromatographed on SiO_2 with $CHCl_3$. The first fraction consisted of 8, the second one gave an additional amount of 9. Compound 8 was recrystallized from CCl_4, needles, M.p. 175-7°, yield 23%. IR: 2230 (CN), 1710 (C=O), 1600 (C=C), 1160, 1120, 1100 (CF_3S); ^1H NMR ($CDCl_3$) 1.1-2.5 (m,16H); 3.7 (m,1H, between rings); 5.0 (t,1H,$CHSCF_3$); ^{19}F NMR 40.9; UV λ_{max} 252.5 ε_{max} 11600. Analysis: Found: C, 58.0; H, 5.0; N, 11.0; S, 8.3%. $C_{19}H_{18}N_3OSF_3$ requires C, 58.00; H, 4.61; N, 10.68; S, 8.15%.

Compound 9, needles, M.p. 198-199°, yield 51.5%. IR: 3380, 3300, 3200 (NH_2), 2210 (CN), 1650 (C=C), 1580 (NH_2), 1130, 1115, 1105 (CF_3S); ^1H NMR ($CDCl_3$) 1.1-2.5 (m,16H); 4.25 (s,1H,$CHSCF_3$); 5.47 (bs,2H,NH_2); ^{19}F NMR 41.86; UV λ_{max}328.9 nm ε_{max} 4900, λ_{max} 222.2 ε_{max} 12900. Analysis: Found: C, 58.4; H, 4.9; N, 14.3; S, 8.1%. $C_{19}H_{19}N_4SF_3$ requires C, 58.15; H, 4.88; N, 14.28; S, 8.17%.

ACKNOWLEDGEMENTS

The experimental part of this work was done at Inorganic Chemistry Department II of Ruhr University in Bochum within the cooperation programme between Ruhr and Jagiellonian Universities. The author thanks Professor Alois Haas for his help with the realization of this project.

REFERENCES

1 M.Adamczyk, J.Mirek, M.Mokrosz, Synthesis (1980) 916.
2 M.Adamczyk, M.Mokrosz, Synthesis (1981) 802.
3 M.Mokrosz, Pol.J.Chem., in press.
4 M.J.Mokrosz, J.L.Mokrosz, Chemica Scripta, 25 (1985) 162.