Tetrahedron Vol. 38, No. 2, pp. 287 to 289, 1982
Printed in Great Britain.

0040–4020/82/020287–03\$03.00/0
Pergamon Press Ltd.

THE NITRILE FUNCTION OF TETRACYANOETHYLENE AS DIENOPHILE IN DIELS–ALDER REACTIONS[1]

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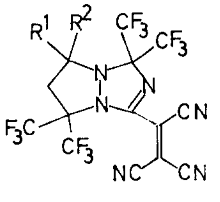
(*Received in Germany* 16 *June* 1981)

Abstract—N - [2,2,2-Trifluoro - 1 - trifluoromethyl(ethylidene)] - thiocarboxamides react with tetracyanoethylene to give [4,4 - bis(trifluoromethyl) - 4H - 1,3,5 - thiadiazin - 2 - yl]ethylenetricarbonitriles and 1,2 - bis[4,4 - bis(trifluoromethyl) - 4H - 1,3,5 - thiadiazin - 2 - yl]ethylenedicarbonitriles. The spectral data of the new compounds are discussed (IR, ^{1}H NMR, ^{19}F NMR and ^{13}C NMR).

Addition and cycloaddition reactions of tetracyanoethylene (TCNE) proceed with high site selectivity at the carbon–carbon double bond.[2–6] Examples of [3+2] cycloaddition reactions where a nitrile function of TCNE reacts as a dipolarophile are rare. 2 - [3,3 - Bis - (trifluoromethyl) - 1 - pyrazolin - 1 - ylio] - 1,1,1,3,3,3 - hexafluoro - 2 - propanides, nitrile sulfides, nitrile oxides and C - aryl - N - phenyl nitrones react with TCNE to yield {4,4,8,8 - tetrakis(trifluoromethyl) - 1,3,5 - triazabicyclo[3.3.0]oct - 2 - en - 2 - yl)ethylenetricarbonitriles **1**,[7] (1,2,4 - thiadiazol - 5 - yl)ethylenetricarbonitriles **2**,[8] (1,2,4 - -oxadiazol - 5 - yl)ethylenetricarbonitriles **3**[8,9] and (3 - aryl - 2 - phenyl - Δ^4 - 1,2,4 - oxadiazolin - 5 - yl)ethylenetricarbonitriles **4**,[10] respectively. In the case of the reaction of nitrile sulfides and nitrile oxides also [2:1] - adducts have been isolated.[8]



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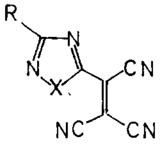
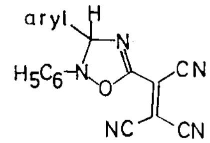


2 X=S
3 X=O



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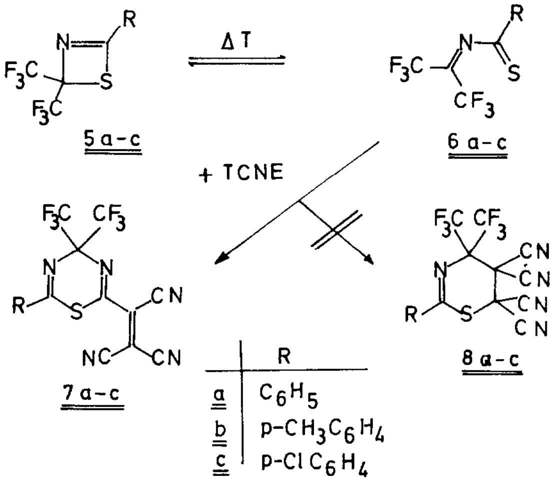
The adduct formed by reaction of diazoacetate and TCNE, originally assigned the structure of a (4 - ethoxycarbonyl - 1H - 1,2,3 - triazol - 5 - yl)ethylenetricarbonitrile,[11] in a reinvestigation, was shown to be in fact the product of a 1,3-dipolar cycloaddition reaction across the carbon–carbon double bond of TCNE.[12]

No examples of Diels–Alder reactions, to our knowledge, have been reported so far, with a nitrile function of TCNE participating as a dienophile.

RESULTS AND DISCUSSION

We have shown that 2,2 - bis(trifluoromethyl) - 2H - 1,3 - thiazetes **5** exist in a thermally mobile valence tautomeric equilibrium with N - [2,2,2 - trifluoro - 1 - trifluoromethyl(ethylidene)]thiocarboxamides **6**. The latter can be trapped by various dienophiles.[13,14] From the reaction of **6** with TCNE a [1:1]- and a [2:1]-adduct can be isolated.



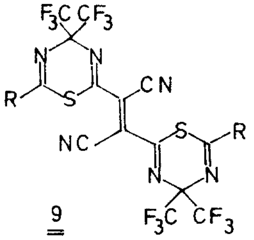
	R
a	C_6H_5
b	p-$CH_3C_6H_4$
c	p-Cl C_6H_4

The colour of the products, yellow to ochre-brown, is not consistent with structure **8**, which is expected to be colourless. The [1:1]-adducts show IR absorptions at 1655–1660 cm^{-1}; 4,4 - bis(trifluoromethyl) - 5,6 - dihydro - 4H - 1,3 - thiazines, formed by reaction of **6** with olefins, enol ethers and enamines do not show any IR absorption in the double bond region at lower wavelength than 1605 cm^{-1}.[13] On the other hand 4,4 - bis(trifluoromethyl) - 4H - 1,3,5 - triadiazines, synthesized by trapping **6** with nitriles, give rise to a strong absorption at 1640–1655 cm^{-1}.[13] A singlet at −1.7 ppm in the ^{19}F NMR spectra of the [1:1]-adducts for the two magnetically equivalent trifluoromethyl groups is characteristic for a $\rangle C(CF_3)_2$ moiety being flanked by two heteroatoms.[13,15–19] The mass spectrometric fragmentation pattern $[M]^{+\cdot}$, $[M–CF_3]^+$, [M–

TCNE]$^{+\cdot}$, [M-RCN]$^{+\cdot}$, [$F_3C)_2C$-N≡C-R]$^{+\cdot}$, [M-RCN, -CF_3]$^+$, [RC≡S]$^+$, [RC≡N]$^{+\cdot}$, especially the fragments [M-RCN, -$(NC)_2C{=}C(CN)$]$^+$ and [$(NC)_2C{=}C(CN)$]$^+$ strongly support structure **7**.

Unequivocal evidence for structure **7** comes from the ^{13}C NMR data. Besides the signals for the substituent R and the two magnetically equivalent trifluoromethyl groups, resonance absorptions for eight different carbon atoms are observed; this finding only can be reconciled with structure **7**. In compounds of type **8**, besides R and the two trifluoromethyl groups, only six nonequivalent carbon atoms are present. A septet at 84 ($^2\underline{J}_{FC} = 30$ Hz), a quartet at 122 ppm ($^1\underline{J}_{FC} = 289$ Hz) are typical for a $(F_3C)_2C{<}^{N=}_{N=}$ moiety.[20] Resonance absorptions at $\delta =$ 162, 158 and 112.6, 112.0, 110.5 ppm demonstrate the presence of two $-C{\genfrac{}{}{0pt}{}{/\!\!/ N-}{\setminus S-}}$ and three –C≡N functions, respectively. TCNE absorbs at 107.9 ($\underline{C}$≡N) and 111.7 ppm ($={\underline{C}}{<}$). The two exocyclic sp^2 carbon atoms give rise to signals at $\delta = 103$ and 135 ppm. No other resonance absorption can be found at higher field than 103 ppm, proving the absence of any other sp^3 carbon atoms in the adducts.

The observation that the [1:1]-adducts can be converted into symmetric [2:1]-adducts provides chemical evidence for the proposed structure **7**. From the three possible structures **9**, **10** and **11** of the [2:1]-adducts, we prefer **9** since the *trans* C≡N group should be the one preferentially attacked in a second cycloaddition step.



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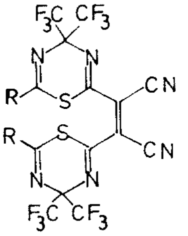

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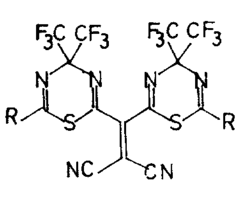

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The νC≡N absorption of compounds **9** is very weak, ^1H and ^{19}F NMR data are similar to those obtained for compounds **7**. The mass spectra show the following breakdown pattern: [M]$^{+\cdot}$, [M-CF_3]$^+$, [M-RCN]$^{+\cdot}$, [M-RCN, -CF_3]$^+$, [M-2RCN]$^{+\cdot}$, [M-2RCN, -CF_3]$^+$, [M-2RCN, -2CF_3]$^+$, [$C_9F_6N_3S_2$]$^+$, [$(F_3C)_2C$=N-CR=S]$^{+\cdot}$, [M-RCN, -TCNE]$^{+\cdot}$, [$(F_3C)_2C$-N≡C-R]$^{+\cdot}$, [M-RCN, -TCNE, -CF_3]$^+$, [$(F_3C)_2C$=N-C≡S]$^+$, [C_3F_6N]$^+$, [RC≡S]$^+$, [$(NC)_2C{=}C(CN)C{\equiv}S$]$^+$, [RCN]$^{+\cdot}$.

Attempts to detect Diels-Alder adducts in the crude reaction products from **6** and TCNE where the carbon-carbon double bond of TCNE functions as dienophile have been unsuccessful so far.

EXPERIMENTAL

IR spectra were measured on a Perkin-Elmer 237 apparatus. ^1H NMR spectra were recorded with a Varian A 60 (Me_4Si as internal standard), ^{19}F NMR spectra with a Jeol C 60 HL at 56.45 MHz (F_3CCOOH as external standard; ^{19}F NMR chemical shifts low field from F_3CCOOH have a negative sign[21]), and ^{13}C NMR spectra with a Bruker WP 200 instrument (Me_4Si as internal standard). Mass spectra were obtained on a AEI MS 9 spectrometer at 70 eV. M. ps. were determined in a Büchi capillary m.p. apparatus and are uncorrected.

Commercially available tetracyanoethylene (TCNE), EGA-Chemie, was sublimed before use.

Trapping reactions of N - [2,2,2 - Trifluoro - 1 - trifluoromethyl(ethylidene)]thiocarboxamides with TCNE

General procedure. A solution of 10 mmol 2,2 - bis(trifluoromethyl) - 2H - 1,3 - thiazete **5**[13] and 1.28 g (10 mmol) TCNE in 25 ml of absolute xylene stirred under N_2 was heated at 120–130° for 48 h. After cooling to room temp the solvent was removed *in vacuo*, the remaining reaction mixture was separated by selective solvent extraction with petroleum ether (fraction 90–110°). [4,4 - Bis(trifluoromethyl) - 4H - 1,3,5 - thiadiazin - 2 - yl)]ethylenetricarbonitriles (**7**) are slightly more soluble than 1,2 - bis[4,4 - bis(trifluoromethyl) - 4H - 1,3,5 - thiadiazin - 2 - yl)]ethylenedicarbonitriles (**9**).

[6 - *Phenyl* - 4,4 - *bis*(*trifluoromethyl*) - 4*H* - 1,3,5 - *thiadiazin* - 2 - *yl*)]*ethylenetricarbonitrile* (**7a**)

Yield 2.48 g (60%); m.p. 162–163°. IR (KBr): 2233, 1658, 1578 cm^{-1}. ^1H NMR (D_6-acetone): $\delta = 7.43$–7.83 m (3H, Ar $\underline{H}$), 7.88–8.20 m (2H, Ar $\underline{H}$). ^{19}F NMR (D_6-acetone): $\delta = -1.7$ s [6F, $C(C\underline{F}_3)_2$]. ^{13}C NMR (D_6-acetone): $\delta = 84.3$ sept., $^2J_{FC} = 30$ Hz ($\underline{C}$–4), 103.2 [$C{=}\underline{C}(CN)_2$], 110.5, 112.0, 112.6 (3$\underline{C}$≡N), 122.3 q, $^1J_{FC} = 289$ Hz (2$\underline{C}F_3$), 128.3, 130.5, 135.1, 135.5 (Ar $\underline{C}$), 135.3 [$\underline{C}(CN){=}C(CN)_2$], 158.5 ($\underline{C}$–2), 162.2 ($\underline{C}$–6). (Found: C, 46.47; H, 1.49; N, 16.87. $C_{16}H_5F_6N_5S$ requires: C, 46.50; H, 1.22; N, 16.94%). Mass spectrum: $M^{+\cdot} = 413$.

1,2 - *Bis*[6 - *phenyl* - 4,4 - *bis*(*trifluoromethyl*) - 4*H* - 1,3,5 - *thiadiazin* - 2 - *yl*]*ethylenedicarbonitrile* (**9a**)

Yield 0.21 g (6%); m.p. 239°. IR (KBr): 2230, 1647, 1597, 1579 cm^{-1}. ^1H NMR (tetrahydrofurane): $\delta = 7.40$–7.78 m (6H, Ar $\underline{H}$), 7.93–8.22 m (4H, Ar $\underline{H}$). ^{19}F NMR (tetrahydrofurane): $\delta = -2.1$ s [12F, $2C(C\underline{F}_3)_2$]. (Found: C, 44.90; H, 1.60; N, 12.03. $C_{26}H_{10}F_{12}N_6S_2$ requires: C, 44.71; H, 1.44; N, 12.03%). Mass spectrum: $M^{+\cdot} = 698$.

[6 - (4 -*Methylphenyl*) - 4,4 - *bis*(*trifluoromethyl*) - 4*H* - 1,3,5 - *thiadiazin* - 2 - *yl*]*ethylenetricarbonitrile* (**7b**)

Yield 2.35 g (55%); m.p. 158–160°. IR (KBr): 2232, 1657, 1607 cm^{-1}. ^1H NMR (D_6-acetone): $\delta = 2.45$ s (3H, $C\underline{H}_3$), 7.30–7.58 m (2H, Ar $\underline{H}$), 7.82–8.10 m (2H, Ar $\underline{H}$), ^{19}F NMR (D_6-acetone): $\delta = -1.7$ s [6F, $C(C\underline{F}_3)_2$]. ^{13}C NMR (D_6-acetone): $\delta =$ 21.6 ($\underline{C}H_3$), 84.3 Sept., $^2J_{FC} = 30$ Hz ($\underline{C}$–4), 103.2 [$C{=}C(CN)_2$], 110.5, 112.0, 112.6 (3$\underline{C}$≡N), 122.3 q, $^1J_{FC} = 289$ Hz (2$\underline{C}F_3$), 128.3, 131.1, 132.2, 146.8 (Ar $\underline{C}$), 135.8 [$\underline{C}(CN){=}C(CN)_2$], 158.2 ($\underline{C}$–2), 161.7 ($\underline{C}$–6). (Found: C, 47.86; H, 1.78; N, 16.31. $C_{17}H_7F_6N_5S$ requires: C, 47.78; H, 1.65; N, 16.39%). Mass spectrum: $M^{+\cdot} =$ 427.

[6 - (4 - *Chlorophenyl*) - 4,4 - *bis*(*trifluoromethyl*) - 4*H* - 1,3,5 - *thiadiazin* - 2 - *yl*]*ethylenetricarbonitrile* (**7c**)

Yield 2.28 g (51%); m.p. 140–141°. IR (KBr): 2233, 1660, 1642, 1584 cm^{-1}. ^1H NMR (D_6-acetone): $\delta = 7.57$–7.82 m (2H, Ar $\underline{H}$), 7.97–8.22 m (2H, Ar $\underline{H}$). ^{19}F NMR (D_6-acetone): $\delta = -1.75$ s [6F, $C(C\underline{F}_3)_2$]. ^{13}C NMR (D_6-acetone): $\delta = 84.4$ sept., $^2J_{FC} = 30$ Hz ($\underline{C}$–4), 103.2 [$C{=}\underline{C}(CN)_2$], 110.5, 112.0, 112.6 (3$\underline{C}$≡N), 122.2 q, $^1J_{FC} = 289$ Hz (2$\underline{C}F_3$), 130.0, 130.7, 133.5, 141.3 (Ar $\underline{C}$), 135.7 [$\underline{C}(CN){=}C(CN)_2$], 157.9 ($\underline{C}$–2), 161.5 ($\underline{C}$–6). (Found: C, 43.11; H, 1.06; N, 15.42. $C_{16}H_4ClF_6N_5S$ requires: C, 42.92; H, 0.90; N, 15.65%). Mass spectrum: $M^{+\cdot} = 447$.

1,2 - *Bis*[6 - (4 - *chlorophenyl*) - 4,4 - *bis*(*trifluoromethyl*) - 4*H* - 1,3,5 - *thiadiazin* - 2 - *yl*] - *ethylenedicarbonitrile* (**9c**)

Yield 0.28 g (7%); m.p. 227°; IR (KBr): 2232, 1657, 1588 cm^{-1}.

^1H NMR (tetrahydrofurane): $\delta = 7.50$–7.73 m (4H, Ar $\underline{H}$), 7.95–8.17 m (4H, Ar $\underline{H}$). ^{19}F NMR (tetrahydrofurane): $\delta = -2.2$ s [12F, 2C($C\underline{F}_3$)$_2$]. (Found: C, 40.85; H, 1.24; N, 10.89. $C_{26}H_8Cl_2F_{12}N_6S_2$ requires: C, 40.69; H, 1.05; N, 10.95%). Mass spectrum: $M^{\dagger} = 766$.

Acknowledgement—This work was supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie. We thank Dr. G. R. Coraor, E. I. du Pont de Nemours & Co. Inc., Wilmington, Delaware, U.S.A., for a generous gift of hexafluoroacetone.

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