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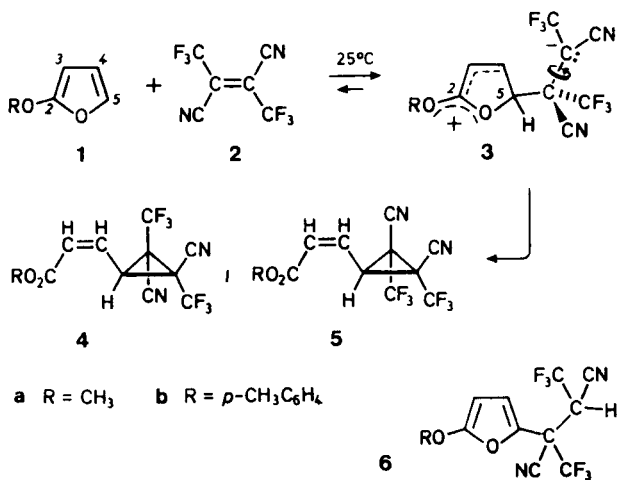
*Dedicated to Professor Jan Thiesing, Darmstadt,
on the occasion of his seventieth birthday*

2-Methoxyfuran and 2-*p*-toloxyfuran were attacked at the 5-position by tetracyanoethylene or the super-electrophilic 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile affording (*Z*)-3-cyclopropylacrylic esters, substituted in the 3-membered ring. Initially formed zwitterions undergo simultaneous opening of the furan and closure of the cyclopropane ring. In the presence of pyridine, 1,3-prototropy converts the zwitterion to 5-substitution products of the furans.

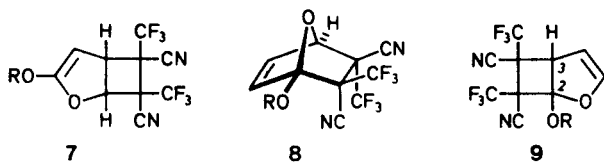
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Introduction.

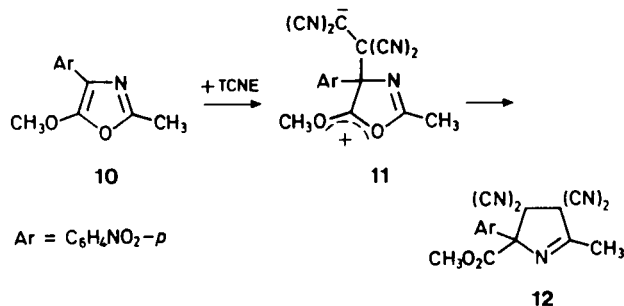
We reported recently on a novel ring opening of donor-substituted furans **1** with the electrophilic 2,3-bis(trifluoromethyl)fumaronitrile (**2**) furnishing (*Z*)-3-cyclopropylacrylic esters **4** and **5**, substituted by pairs of CN and CF₃ groups in the three-membered ring [2]. Electrophilic attack at the 5-position of **1** led to the zwitterion **3** as a plausible intermediate which undergoes intramolecular



nucleophilic substitution; the ester group functions as a leaving group. Under base catalysis, the opening of the heteroring is suppressed in favor of a 1,3-prototropy providing the disubstituted furans **6**. The formation of **4** and **5** from the reactants is for 2-methoxyfuran (**1a**) 85 times faster than for the less nucleophilic 2-*p*-toloxyfuran (**1b**); 94% conversion was observed for the formation of **4b** and **5b** from **1b** and **2** after 14 days in deuteriochloroform at 25°, 6% of **2** still being unconsumed.



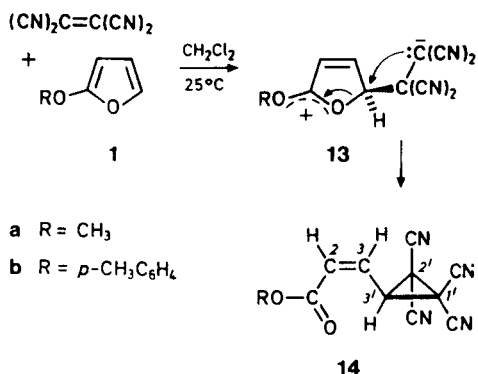
When the reactions were monitored by ¹⁹F nmr spectroscopy after shorter periods, a rapid equilibration of the reactants with (2+2) and/or (4+2) cycloadducts was revealed [3]. Adducts **7** and **8** could conceivably be formed *via* the same zwitterionic intermediate as **4-6**. However, **9** would require an initial attack at position 3 of **1**. *Cis*-annellation would allow **7-9** in four diastereoisomers each. Diagnosed by the F,F coupling, four *trans*- and one *cis*-adduct with respect to the CF₃ groups occurred. Measurements of the equilibrium constants over a range of 90° provided cycloaddition enthalpies and entropies [3].



Ibata *et al.* [4,5] described "abnormal Diels-Alder reactions" of substituted 5-alkoxyoxazoles with tetracyanoethylene; *e.g.*, **10** was converted to 83% of adduct **12** with **11** and a second intermediate, a nitrilium betaine, being proposed. The major difference to the reaction observed by us lies in the stabilization of the initially formed zwitterion. Analogous reactions of 5-alkoxyoxazoles with *N*-phenyl-1,2,4-triazoline-3,5-dione [6], thioacetaldehyde [7], diethyl azodicarboxylate [8], and nitrosobenzene [9] were reported.

Results and Discussion.

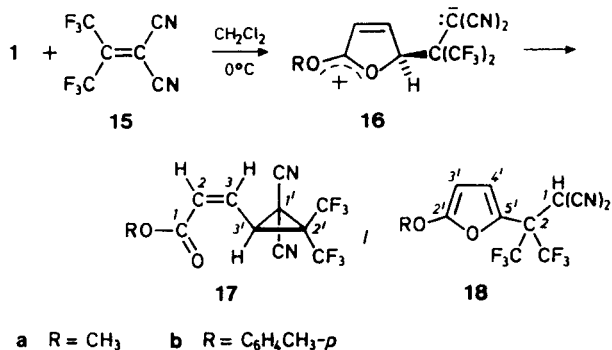
Tetracyanoethylene (TCNE) exceeds **2** in electrophilic activity. The deep violet charge-transfer (CT) color with 2-methoxyfuran (**1a**) disappeared in a few seconds, and 67% of the crystalline product **14a** was isolated. In the ¹H



nmr spectrum, two vinyl protons at δ 6.20 and 6.58 show with 11.0 Hz a *cis*-vinylic coupling. These protons absorb in 2-methoxyfuran (**1a**) itself at δ 5.07 (3-H) and 6.20 (4-H) and couple with 3.5 Hz. The 5-H of **1a** (δ 6.80) is converted to the high-field 3'-H (δ 4.59) at the cyclopropane ring of **14a**. In accordance with a plane of symmetry in **14a**, the δ_c of C-1' and C-2' are identical, and the CN groups are pairwise so; δ_c 37.8 for C-1' and C-2' and 23.0 for C-3' are the high-field absorptions expected for cyclopropane C-atoms. Amusingly, δ_c 161.9 for C-2 of furan **1a** comes close to 165.1 for the carbonyl C-atom of adduct **14a**, but the ir stretching frequency of the carbonyl group at 1717 cm⁻¹ for **14a** is that of an α,β -unsaturated ester.

Correspondingly, 2-*p*-tolylxyfuran (**1b**) was converted by TCNE into the (*Z*)-3-cyclopropyl-substituted *p*-tolyl acrylate **14b**. The fading of the CT color - somewhat slower than for **1a** - signaled a still fast consumption of TCNE. In contrast to the reaction of **1** with **2** [3], eventual (2+2) or (4+2) cycloadducts of type **7-9** must be of fleeting existence.

In the mass spectra, $m/z = 131$ is the base peak for adduct **14a** and occurs with 32% for **14b**; probably it is $(\text{CN})_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{C}\equiv\text{O}^+$, disclosing the main fragmentation of the radical cation.



2,2-Bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (**15**) is a "superelectrophile" [10]; its (2+2) cycloaddition with butyl vinyl ether is 2 400 times faster than that of TCNE (benzene, 25°) and exceeds the rate of the isomeric **2** 42 000-fold [11,12]. In the interaction of furan **1b** with **15**

in dichloromethane at 0°, the yellow CT color disappeared in seconds, and the CT color became hardly visible in the reaction of the more nucleophilic furan **1a** with **15**. The ¹H nmr analysis indicated a 90:10 mixture of **17a** and **18a** as well as a ratio of 86:14 of **17b** and **18b** (dichloromethane, 0°; ratio 95:5 in deuteriochloroform), respectively. Thus, despite the high rate, 1,3-prototropy of the assumed intermediate **16** can compete to a minor extent with the intramolecular nucleophilic substitution furnishing **17**. In the presence of 1.9 equivalents of pyridine as a base, furan **1a** afforded only **18a**, the result of electrophilic aromatic substitution, whereas **1b** gave rise to **17b** and **18b** in a 10:90 ratio.

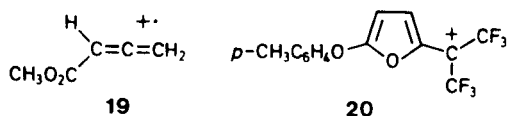
The purification of **17** was achieved by thick-layer chromatography (tlc) on silica gel and subsequent distillation at 10⁻³ torr; **17a** was obtained crystalline, **17b** was oily.

The acrylic esters **17** lack an element of symmetry. In the ¹³C nmr spectrum of **17b**, the singlet at δ 14.5 was assigned to C-1' and the septet at 43.8 with ²J_{C,F} 33.6 Hz to C-2'; C-3' absorbs at δ 32.1. With δ_c 107.5 and 108.9 the CN groups absorb slightly different, as do the CF₃ groups with 120.0 and 121.1 (¹J_{C,F} = 281.1 Hz).

The vinylic 3-H of **17b** is not only coupled by 2-H ($J_{2,3} = 11.1$ Hz) and 3'-H ($J_{3,3'} = 6.7$ Hz); in addition, the neighboring CF₃ group splits the doublet of doublets into quartets with $J_{3,F} = 2.2$ Hz. Due to the 1:3 ratio of two J values, the expected 12 lines perfectly appear at δ_H 6.26. Fluorine couplings are transmitted through space; only the *cis*-CF₃ group is engaged in this interaction. F,F coupling generates quartets at $\delta_F -59.8$ and -64.8 with ⁴J_{F,F} = 8.7 Hz in the ¹⁹F nmr spectrum; only the first is further split by 3-H into doublets. Characteristically, this *cis*-CF₃ group is deshielded by two *cis*-vicinal substituents on the cyclopropane ring and occurs at lower field. The nmr assignments are buttressed by corresponding ones for the methyl acrylate **17a**.

The cyano group stabilizes the carbanion to a higher extent than CF₃. The structure **16** of the intermediate zwitterion contains a terminal anion of malononitrile type. It was confirmed by the nmr spectra of **18** which originates from the pyridine-catalyzed 1,3-prototropy. Due to a plane of symmetry, the CF₃ groups occur as a singlet at $\delta_F -67.1$ (**18a**) and -66.7 (**18b**), not coupled by the aliphatic proton (1-H). The broadened singlets at δ_H 4.81 (**18a**) and 4.85 (**18b**) - slow exchange by deuterium oxide - were assigned to 1-H. In the study of ene products from alkenes and **15** [13], the proton of $-\text{C}(\text{CF}_3)_2-\text{C}(\text{CN})_2\text{H}$ was found as singlet at δ_H 4.3-4.8, whereas $-\text{C}(\text{CN})_2-\text{C}(\text{CF}_3)_2\text{H}$ gave rise to a septet at δ_H 3.4-3.8.

The 3'-H and 4'-H signals of **18** are of furan type, e.g., two doublets at δ_H 5.32 and 6.72 with $J = 3.6$ Hz for **18a** ($J_{3,4} = 3.5$ Hz for **1a**); the doublet of 4'-H is broadened by an unresolved long range H,F coupling.



The base peak in the mass spectrum of methyl ester **17a** is $m/z = 98$, probably the radical cation of methyl allene-carboxylate (**19**), suggesting the neutral **15** as the second fragment. In the *p*-tolyl ester **17b**, the radical cation of *p*-cresol (m/z 108) constitutes the base peak and $M^+ - C_7H_7O$ (m/z 281) occurred with 14%. The furan ring in **18b** induces another type of fragmentation. The benzyl type cation **20**, highly stabilized by the oxygen functions, is the base peak and results from the elimination of $CH(CN)_2$.

The intramolecular substitution of zwitterions **13** and **16** offers a satisfactory mechanistic pathway to **14** and **17**; the carboxylic ester acts as a leaving group. The reversible formation of cycloadducts of type **7-9** (observed with **2**) is conceivable here, too. The ^{19}F nmr spectra, taken after 10 minutes reaction of **1a** or **1b** with **16**, reveal complete formation of the final products, thus reducing the passing occurrence of cycloadducts to even shorter periods.

EXPERIMENTAL

Instruments and Techniques.

The nmr spectra (in deuteriochloroform, unless otherwise stated) were recorded on a Varian VXR 400S spectrometer: 1H 400 MHz, ^{13}C 100 MHz, ^{19}F 376 MHz. The J values in ^{13}C spectra refer to C,H couplings, unless stated otherwise. Quantitative ^{19}F nmr analyses were carried out with trifluoroanisole ($C_6H_5OCF_3$) as a weight standard. Infrared spectra (potassium bromide disks) were recorded on a Bruker IFS 45 Fourier spectrometer, mass spectra on a Finigan MAT 90 instrument with 70 eV.

Silica gel Merck 60 PF₂₅₄, 2 mm, served the thick-layer chromatography (tlc). High-vacuum (hv) distillation was carried out in microflasks under 10^{-3} torr.

Methyl (*Z*)-3-(1',1',2',2'-Tetracyanocycloprop-3'-yl)acrylate (**14a**).

2-Methoxyfuran (**1a**, Aldrich, freshly distilled, 216 mg, 2.2 mmoles) was added dropwise to the stirred solution of 256 mg (2.0 mmoles) of tetracyanoethylene (TCNE) in 4 ml of dichloromethane during 15 minutes at room temperature. After 30 minutes the solvent was removed, and the light yellow residue crystallized from ethanol, 305 mg (67%) of colorless prisms, mp 159-161° dec (pentane/ether); ir: ν 699, 725 (*cis*-CH=CH wagging), 1203, 1258 (C-O), 1646 (C=C), 1717 (C=O), 2264 cm^{-1} weak (C≡N); 1H nmr (acetone- d_6): δ 3.87 (s, 3H, OCH₃), 4.59 (dd, 3'-H), 6.20 (dd, 2-H), 6.58 (dd, 3-H) with $J_{2,3} = 11.0$ Hz, $J_{2,3'} = 1.8$ Hz, $J_{3,3'} = 5.8$ Hz; ^{13}C nmr (acetone- d_6 , 1H -decoupled, dept): δ 23.0 (C-3'), 37.8 (C-1', C-2'), 52.6 (OCH₃), 108.0 (2 CN), 109.5 (2 CN), 130.3, 131.5 (C-2 and C-3), 165.1 (C=O); ms (50°): m/z (%) 226 (M^+ , 0.1), 195 (M-OCH₃, 21); ^{13}C Calcd. 2.4, Found 2.2%, 162 (M-C(CN)₂, 37), 131 (162 -OCH₃, 100); ^{13}C Calcd. 8, Found 9%, 103 (131 -CO, 27), 98 (M -TCNE, 27), 76 (radical cation of NC-C≡C-CN, 28).

Anal. Calcd. for $C_{11}H_6N_4O_2$ (226.2): C, 58.41; H, 2.67; N, 24.77. Found: C, 58.49; H, 2.87; N, 24.55.

p-Tolyl (*Z*)-3-(1',1',2',2'-Tetracyanocycloprop-3'-yl)acrylate (**14b**).

Starting from 2.2 mmoles of 2-*p*-tolylxyfuran (**1b**) [14] and 2.0 mmoles of TCNE, 560 mg (93%) of **14b** were analogously obtained, colorless, mp 190-192° dec (acetone). The decolorization of the violet CT color was somewhat slower here; ir: ν 695, 726 (*cis*-CH=CH w), 782, 802, 835 (C_6H_4 w), 1166, 1175, 1198, 1231 (C-O), 1508 (C_6H_4 ring), 1642 (C=C), 1738 (C=O), 2270 cm^{-1} w (C≡N); 1H nmr (acetone- d_6): δ 2.35 (s, 3H, CH₃), 4.84 (dd, 3'-H), 6.58 (dd, 3-H), 6.91 (dd, 2-H) with $J_{2,3} = 11.2$ Hz, $J_{2,3'} = 2.0$ Hz, $J_{3,3'} = 6.9$ Hz, 7.1-7.3 (AA'BB', C_6H_4); ^{13}C nmr (acetone- d_6 , 1H -decoupled, dept): δ 20.8 (CH₃), 24.5 (C-3'), 38.8 (C-1', C-2'), 109.6 and 111.0 (2 CN each), 122.0, 130.4 (4 arom CH), 131.1, 133.9 (C-2, C-3), 136.9, 149.1 (2 arom C_q), 164.3 (C=O); ms (50°): m/z (%) 302 (M^+ , 3), 238 (M -C(CN)₂, 10); ^{13}C Calcd. 1.5, Found 1.4%, 131 (238 -OC₇H₇, 32); ^{13}C Calcd. 2.5, Found 2.2%, 108 ($CH_3C_6H_4OH$, 100), 107 ($CH_3C_6H_4O$, 52).

Anal. Calcd. for $C_{17}H_{10}N_4O_2$ (303.3): C, 67.54; H, 3.34; N, 18.54. Found: C, 67.46; H, 3.30; N, 18.54.

Methyl (*Z*)-3-[1',1'-Dicyano-2,2'-bis(trifluoromethyl)cycloprop-3'-yl]acrylate (**17a**).

The solution of 2.0 mmoles of furan **1a** in 2 ml of dichloromethane was dropwise added to 428 mg (2.0 mmoles) of 2,2'-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (**15**) [15] in 2 ml of dichloromethane, stirred in an ice-bath. Hv distillation at 70° gave an oil which contained **17a** and **18a** in a 90:10 ratio (1H nmr). Tlc with dichloromethane/petroleum ether (6:4) and renewed hv distillation afforded 454 mg (73%) of **17a** as a colorless oil which solidified, mp 72-73° (pentane, -15°); ir: ν 705, 718 (*cis*-CH=CH w), 1188, 1229, 1253, 1269 (C-F, C-O), 1656 (C=C), 1725 (C=O), 2260 cm^{-1} w (C≡N); 1H nmr: δ 3.84 (s, 3H, OCH₃), 4.40 (dd, 3'-H), 6.14 (ddq, 12 lines, 3-H), 6.42 (dd, 2-H) with $J_{2,3} = 11.0$ Hz, $J_{2,3'} = 1.7$ Hz, $J_{3,3'} = 6.4$ Hz, $J_{3,F} = 2.2$ Hz; ^{13}C nmr (fully coupled): δ 14.7 (s, C-1'), 32.4 (dd, $^1J = 175.6$ Hz, $^2J = 13.2$ Hz, C-3'), 43.7 (septet, $^2J_{C,F} = 34.3$ Hz, C-2'), 52.5 (q, OCH₃), 107.7 (d, $^3J = 4.6$ Hz, CN), 109.3 (d, $^3J = 6.9$ Hz, CN), 120.2 and 120.3 (2 q, $^1J_{C,F} = 280.8$ Hz, 2 CF₃), 129.6 (dd, $^1J = 169.5$ Hz, $^2J = 1.6$ Hz, C-2 or C-3), 130.3 (dd, $^1J = 167.8$ Hz, $^2J = 3.1$ Hz, C-3 or C-2), 165.2 (s, C=O); ^{19}F nmr: δ -59.46 (dq, $^4J_{F,F} = 8.9$ Hz, $^3J_{F,H} \sim 2$ Hz, *cis*-CF₃), -64.45 (q, $^4J_{F,F} = 8.9$ Hz, *trans*-CF₃); ms (25°): m/z (%) 312 (M^+ , 0.3), 281 (M -OCH₃, 47), 98 ($C_5H_6O_2$, 19, 100), 83 (98 -CH₃, 22), 69 (CF₃, 54).

Anal. Calcd. for $C_{11}H_6F_6N_2O_2$ (312.2): C, 42.32; H, 1.94; N, 8.97. Found: C, 42.31; H, 2.02; N, 8.75.

2-(2'-Methoxyfur-5'-yl)-2,2-bis(trifluoromethyl)ethane-1,1-dicarbonitrile (**18a**).

As described for **17a**, 2.0 mmoles of **1a** and 2.2 mmoles of **15** were reacted in dichloromethane at 0°, but now in the presence of 0.20 ml (3.8 mmoles) of pyridine. Hv distillation at 70° provided 583 mg (93%) of **18a** as a colorless oil which crystallized at -20°, prisms (hexane/ether 1:1), mp 33-35°; ir: ν 675, 745, 762 (arom CH w), 1035, 1158, 1225, 1323 (C-O, C-F), 1567, 1613 (furan ring vibr); 2114 cm^{-1} in the film spectrum of the fresh distillate suggested some ketene imine tautomer; 1H nmr: δ 3.90 (s, 3H, OCH₃), 4.81 (br s, 1-H), 5.32 (d, $J = 3.6$ Hz, 3'-H), 6.72 (d, $J = 3.6$ Hz, broadened by H,F coupling 4'-H); ^{13}C nmr (fully coupled): δ 24.2 (br s, C-1), 57.4 (septet, $^2J_{C,F} = 28.4$ Hz, C-2), 58.4 (q, $J = 147.2$ Hz, OCH₃), 82.3 (dd, $^1J = 181.4$, $^2J = 3.6$ Hz, C-3'), 108.2 (s, 2 CN), 117.6 (d septet, $^1J_H = 178.3$ Hz, $^4J_{C,F} = 1.8$ Hz, C-4'), 121.7 (q, $^1J_{C,F} = 287.3$ Hz, 2 CF₃), 126.6 (symm. m, $^2J = ^3J_{C,F} =$

8.3 Hz, C-5'), 163.5 (ddq, 12 lines visible in expanded spectrum, $^2J = 9.4$ Hz, $^3J_{C,H3} = 4.3$ Hz, $^3J = 6.7$ Hz, C-2'); ^{19}F nmr: $\delta -67.1$ (s, F,H coupling unresolved, 2 CF₃).

Anal. Calcd. for C₁₁H₆F₆N₂O₂ (312.2): C, 42.32; H, 1.94; N, 8.97. Found: C, 42.43; H, 2.10; N, 8.94.

p-Tolyl (Z)-3-[1',1'-Dicyano-2',2'-bis(trifluoromethyl)cycloprop-3'-yl]acrylate (**17b**).

The reaction of 2.0 mmoles of **1b** with 2.0 mmoles of **15** at 0° was run as described for **17a**; the yellow CT color disappeared after each drop in a few seconds. After 10 minutes the 1H nmr spectrum indicated consumption of **1b** and formation of **17b** and **18b**; the ratio of 86:14 remained unchanged on hv distillation at 130°. The pure **17b** was obtained by tlc (dichloromethane, petroleum ether 1:1) from the faster moving zone and subsequently hv distilled (colorless oil, 503 mg, 65%); ir (film): ν 693, 710 (*cis*-CH=CH w), 819 (arom CH w), 1174, 1201 (C-F), 1294, 1343 (C-O), 1507, 1552 (conjugated C₆H₄), 1647 (C=C), 1737 (C=O), 2260 cm⁻¹ w (C≡N); 1H nmr: δ 2.35 (s, 3H, CH₃), 4.44 (br d, 3'-H), 6.26 (ddq, 12 lines, 3-H) and 6.61 (dd, 2-H) with $J_{2,3} = 11.1$ Hz, $J_{2,3'} = 1.7$ Hz, $J_{3,3'} = 6.7$ Hz, $J_{3,F} = 2.2$ Hz; 7.00-7.23 (AA'BB', C₆H₄); ^{13}C nmr (fully coupled): δ 14.5 (s, C-1'), 20.9 (qt, $^1J = 126.6$ Hz, $^3J = 4.2$ Hz with 2 *o*-H of tolyl, CH₃), 32.1 (dd, $^1J = 178$ Hz, $^2J = 14.0$ Hz, C-3'), 43.8 (septet, $J_{C,F} = 33.6$ Hz, C-2'), 107.5 (d, $^3J = 4.5$ Hz, CN), 108.9 (d, $^3J = 6.5$ Hz, CN), 120.0, 120.1 (2 q, $^1J_{C,F} = 281.1$, 2 CF₃), 120.9, 130.0, 130.2, 131.3 (4 dd, 2 olefinic and 4 arom CH), 136.4 (q, $^2J = 6.4$ Hz, C-4 of 4-tolyl), 147.7 (s, C-1 of 4-tolyl), 163.4 (d, $^2J = 13.8$ Hz, C=O); ^{19}F nmr: $\delta -59.8$ (qd, $^4J_{F,F} = 8.7$ Hz, $J_{F,H} \sim 2$ Hz, *cis*-CF₃), -64.8 (q, *trans*-CF₃); ms (50°): *m/z* (%) 388 (M⁺, 24); ^{13}C Calcd. 4.6, Found 4.2%, 361 (M -HCN, 11), 281 (M -C₇H₇O, 14), 254 (281 -HCN, 17), 108 (C₇H₇OH, 100%).

Anal. Calcd. for C₁₇H₁₀F₆N₂O₂ (388.3): C, 52.59; H, 2.60; N, 7.22. Found: C, 52.68; H, 2.76; N, 7.33.

We wished to monitor the reaction of 0.48 M **15** with 0.66 M **1b** by ^{19}F nmr in the presence of trifluoroanisole (C₆H₅OCF₃) as a weight standard; 10 minutes were required until the first spectrum was recorded. The electrophile **15** was already consumed, and the comparison of integrals indicated 97% **17b** and 5% **18b** (standard deviation $\pm 4\%$ rel).

2-(2'-*p*-Tolyloxyfur-5'-yl)-2,2-bis(trifluoromethyl)ethane-1,1-dicarbonitrile (**18b**).

The preceding experiment was repeated in the presence of 0.20 ml (3.8 mmoles) of pyridine and furnished a 90:10 mixture of **18b** and **17b** (1H nmr analysis). Because **18b** was not stable on

silica gel, we contented ourselves with the spectral characterization after hv distillation at 130° (610 mg, 79%, oil); ir (film): 733, 845 (arom CH w), 1164, 1207, 1256, 1320 (C-F, C-O), 1505, 1552 (conjugated C₆H₄), 1606, 1628 cm⁻¹ (furan ring), no C≡N; 1H nmr: δ 2.33 (s, 3H, CH₃), 4.85 (br s, slow exchange by deuterium oxide, 1-H), 5.56 (d, $J = 6.7$ Hz, 3'-H), 6.77 (d, $J = 6.7$ Hz, 4'-H), 6.96-7.17 (AA'BB', C₆H₄); ^{13}C nmr (1H -decoupled): 20.7 (CH₃), 24.1 (C-1), 57.4 (septet, $^2J_{C,F} = 28.0$ Hz, C-2), 89.7 (C-3'), 107.9 (2 CN), 117.5 (C-4'), 121.6 (q, $^1J_{C,F} = 288.4$ Hz, 2 CF₃), 128.5 (C-5'), 130.2, 135.0 (4 CH of 4-tolyl), 136.5, 153.4 (C-4 and C-1 of 4-tolyl), 159.5 (C-2'); ^{19}F nmr: 66.7 (s, 2 CF₃); ms (25°): *m/z* (%) 388 (M⁺, 28%), 323 (M -CH(CN)₂, 20), 100, ^{13}C Calcd. 15.7, Found 14.8), 213 (34), 108 (C₇H₇OH, 30), 91 (tropylium, 77).

Anal. Calcd. for C₁₇H₁₀F₆N₂O₂ (388.3): C, 52.59; H, 2.60; N, 7.22. Found: C, 52.55; H, 2.71; N, 7.20.

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REFERENCES AND NOTES

- [1] Present address: Prof. G. Mloston, Department of Organic and Applied Chemistry, University of Lodz, Narutowicza 68, 90-136 Lodz, Poland.
- [2] G. Urrutia-Desmaison, G. Mloston and R. Huisgen, *Tetrahedron Letters*, **35**, 4977 (1994).
- [3] R. Huisgen and G. Mloston, *Tetrahedron Letters*, **35**, 4981 (1994).
- [4] T. Ibata, Y. Isogami, S. Nakano, H. Nakawa and H. Tamura, *J. Chem. Soc., Chem. Commun.*, 1692 (1986).
- [5] T. Ibata, Y. Isogami, H. Nakawa, H. Tamura, H. Suga, X. Shi and H. Fujeda, *Bull. Chem. Soc. Japan*, **65**, 1771 (1992).
- [6] T. Ibata, Y. Isogami and H. Tamura, *Chem. Letters*, 1551 (1988).
- [7] E. Vedejs and S. Fields, *J. Org. Chem.*, **53**, 4663 (1988).
- [8] A. Hassner and B. Fischer, *Tetrahedron*, **45**, 3535 (1989).
- [9] H. Suga and T. Ibata, *Chem. Letters*, 1221 (1991).
- [10] R. Huisgen and R. Brückner, *Tetrahedron Letters*, **31**, 2553 (1990).
- [11] R. Brückner and R. Huisgen, *Tetrahedron Letters*, **31**, 2557 (1990).
- [12] T. Oshima, Univ. of Munich, 1984, unpublished.
- [13] R. Huisgen and R. Brückner, *J. Org. Chem.*, **56**, 1679 (1991).
- [14] A. F. Oleinik, K. J. Nowickij, L. V. Bratceva, T. A. Guskowa, G. N. Piershin, A. J. Kravtchenko and W. A. Tschernow, *Khim.-Farm. Zh.*, **10**, 65 (1976); *Chem. Abstr.*, **85**, 142934m (1976).
- [15] W. J. Middleton, *J. Org. Chem.*, **30**, 1402 (1965).