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ELECTROPHILIC SUBSTITUTIONS BY 2,2-BIS(TRIFLUOROMETHYL)ETHYLENE-1,1-DICARBONITRILE VIA ADDITION¹

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Summary The interaction of the title compound (BTF) with unsaturated nucleophiles (ketene dithioacetals, α -substituted vinyl ethers, N-vinylcarboxamides, enols, furans, N-methylpyrrole, N-methylindole) effects substitution of vinylic or aromatic H by -C(CF₃)₂-CH(CN)₂.

The highly electrophilic 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (BTF) ² converts nucleophilic unsaturated compounds into carbocationic intermediates by two ways, either addition to the double bond furnishing a 1,4 zwitterion, $1 \rightarrow 2$, or by hydride abstraction giving rise to an allylic ion pair, $7 \rightarrow 8$.



The 1,4-zwitterion 2 may cyclize to the cyclobutane 3 as observed for enol ethers (X = OR) or thioenol ethers (X = SR) ^{3,4} whereas 1,3 or 1,5 prototropy leads to substitution products without or with shift of the double bond (4, 5). The formation of a type 5 product from α -methylstyrene and BTF ⁵ presumedly offers an example for the 1,5-H shift of zwitterion 2 (X = C₆H₅). Alternatively, the full development of charges in reactions $2 \rightarrow 5$, i. e., the intermediacy of zwitterion 2, can be circumvented



by the 1,5-H shift in concert: the *ene reaction* via **6** with *obligatory double bond shift* is the main pathway for terminal alkenes + BTF⁶.

The abstraction of allylic hydrogen from **7** or **7a** by BTF affords ion pair **8**; recombination at both termini of the allylic cation provides **9** and **10**. This is the favored pathway of BTF interaction with isobutenyl, methallyl, and allyl ethers or sulfides ⁷. CC bond formation may be concerted with the hydride shift. The ene reaction of type **11**, likewise with obligatory shift of the double bond, predominates in treating nonterminal alkenes or allylbenzenes with BTF ⁶.

The pairs 4/5 and 9/10 are formal substitution products of 1 and 7; they result from fundamentally different pathways. The superior stabilization of the carbanion by C=N compared with CF₃ offers a unique probe of distinguishing the two substitution mechanisms by the terminal group, CH(CN)₂ vs. CH(CF₃)₂. Moreover, BTF (E_A = -3.1 eV) exceeds even TCNE (E_A = -2.8 eV) in electrophilicity. We report here some substitutions initiated by the attack of BTF on the carbon of unsaturated compounds (via 2 \rightarrow 4); their common signet is the terminus CH(CN)₂. Substitutions via hydride abstraction (7 \rightarrow 10) are the subject of the accompanying paper.



Vinylic substitution with BTF via 1,4 zwitterion is often preceded by cyclobutane formation (thermodynamic vs. kinetic control). High stabilization of the carbocation entails not only fast generation of **2** from the reactants, but also rapid ring opening of the cyclobutane back to **2**. On reacting *ketene diethyldithioacetal* at room temperature, the ¹H NMR spectrum revealed only **12b** which isomerized during high-vacuum distillation to **14b** - probably by acid-base catalyzed 1,3 proton shift in **13b**.

The ¹H NMR signals of the enantiotopic groups SC_2H_5 in **12b** became different in the conversion to **14b**, and the vinylic 3-H (slightly broadened by H,F coupling) occurred at δ 5.73⁸. The singlet of the acidic 1-H appeared at δ 6.81 for **14b** and exchanged with CH₃OD; the ¹⁹F singlet at δ -67.7 established enantiotopic CF₃ groups. The base peak in the MS of **14b** is M⁺ - CH(CN)₂, i.e., **15**, thus revealing the major fragmentation pathway.

 α -Methoxystyrene and BTF produced the cycloadduct **16a** (δ 2.91 and 3.48 for 3-H₂, 2 m at δ_{F} -68.4, -69.0) at r.t. within a few sec (63%, mp 111.5 - 112°C); catalysis by CF₃CO₂H converted it to **17a** (80% after distillation at 50°C/10⁻⁴ Torr, s δ_{H} 4.77 for 3-H, 2 s δ_{F} -68.8 and -67.8 in 96:4 ratio for *E/Z*). 2-Methoxypropene combined with BTF at 0°C in 10 sec, and distillation provided 86% of (*Z*)- and (*E*)-**17c**

in a 3:1 ratio (δ_{H} OCH₃ 3.73, 3.60; C-CH₃ 2.03, 2.89; 3-H 4.39, 4.26). In the MS of **17**, again M⁺ – CH(CN)₂ emerged: 83% in **b**, 100% in **c**.



Analogous substitution products were obtained from *N*-vinylacetanilide (89% **18**), *N*-vinylpyrrolidone (72% **19** after 10 sec), and 3,4-dihydro-2H-pyran (70% **20**, mp 38.5 - 40°C). The vinylic 3-H and 4-H of **18** and **19** appeared as wide-spaced AX spectra typical for acceptor-donor substituted ethylenes (\mathcal{E}_{H} 4.30 and 8.26 for **18**, 4.81 and 7.61 for **19**); $J_{3.4}$ 14.8 and 15.0 Hz established the (*E*) configuration.



The enol forms of ketones are electron-rich olefins of type 1 (X = OH) The slow reactions of acetone, acetophenone and cyclopentanone afforded the substitution products 21-23. The δ (1-H) singlets at 5.78 - 5.96, their H,D exchange with CH₃OD as well as the multiplicity of the CF₃ signals (s for 21 and 22, 2 q for 23, i.e., no H,F coupling) confirm the regiochemistry according to $R_N = C(CF_3)_2$ -CH(CN)₂. The infrared C=O frequencies of the ketones are hardly changed in the BTF adducts. The attack of BTF at the β -C-atom of the enol may take place via a zwitterion 2 (X = OH) or by a one-step ene reaction of type 6. The corresponding reaction of TCNE with ketones requires catalysis by silver or BF₃⁹.

The unit C=C-X in **1** encompasses *aromatic rings*, likewise capable of sustaining a positive charge upon electrophilic attack. TCNE and *N*,*N*-dimethylaniline furnish the red dye **24** ¹⁰. The primary product **25** is isolable ¹¹ and its conversion to **24** is base-catalyzed. It is not astounding that the reaction of BTE with aniline stops at **26**².

In contrast to 2-methylfuran, the parent compound was described as unreactive to TCNE ¹². *Furan* slowly combined with BTF (3 months in pentane at r.t.) giving the 2'-substitution product **27** (60% after distill. at 50°C/10⁻³ Torr), not a Diels-Alder adduct. The 1-H (singlet at δ 5.04) is exchanged by CH₃OD. In the ¹⁹F-decoupled ¹H NMR spectrum the aromatic protons were found at δ 6.83 (3'-H), 6.45 (4'-H), and 7.56 (5'-H) as doublets of doublets. The coupling constants ($J_{3,4}$ 3.6, $J_{3,5}$ 0.8, $J_{4,5}$ 3.5 Hz) established three contiguous H, and, thus, the anchoring of R_N at 2'-position. *2-Methylfuran* reacted

faster (63% after 14 d in CH₂Cl₂ at r.t.); 3'-H and 4'-H occurred at δ 6.72 and 6.14 (J 3.5 Hz) in **28**, again in accordance with substitution in the second α -position.



In the interaction of *N*-methylpyrrole with BTF the dark-red color of the CT complex faded in 3 sec, and distillation furnished 78% of the colorless **29** (mp 49-55°C); 2'-substitution was assumed in analogy with **27**. $M^+ - CH(CN)_2$ was the base peak in the MS of **29**. The bisadduct **30**, slowly formed with excess of BTF (26% after 4 weeks in CH₂Cl₂ at r.t.), displayed two pyrrole-H at δ 6.39 and 7.27 as well as two CF₃ singlets; this would be incompatible with a symmetrically disubstituted pyrrole.

N-Methylindole and TCNE afforded the colorless 3-substitution product via a black-purple CT complex ¹³. The quantitatively formed BTF-adduct **31** (mp 116-117°C) was light-violet; on recrystallization, it came out of a dark-violet solution, suggesting some reversal to the CT complex of the reactants.

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