

CYCLOADDITIONS WITH CAPTO-DATIVE OLEFINS, II¹⁾
 TETRAHYDROTHIOPHENES FROM ADDITION OF 2-(TERT-BUTYLTHIO)-ACRYLONITRILE TO DIENOPHILES²⁾

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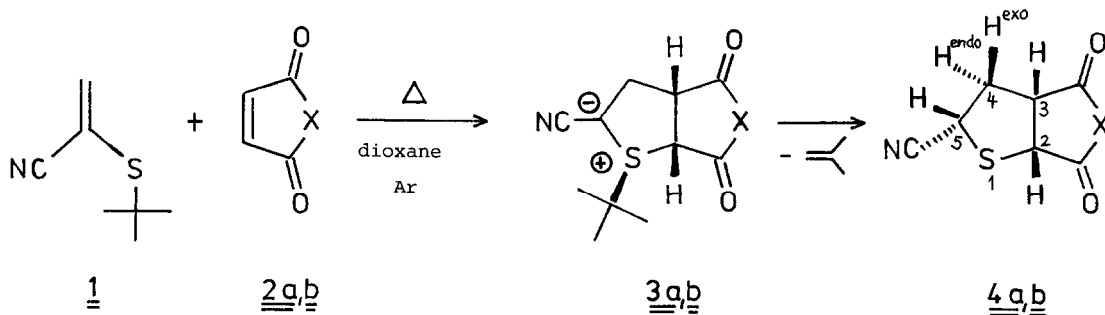
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Summary: With loss of the tert-butyl group, 2-tert-butyl-thioacrylonitrile (1) may be added thermally to N-phenyl maleic imide (2a), maleic anhydride (2b) and other olefins to yield tetrahydrothiophene-2-carbonitriles; from the addition to dimethyl ethyne dicarboxylate, the dihydrothiophene 7 is obtained.

Capto-dative substituent effects³⁾ are a field of considerable current interest^{1,3-8)}. Several groups are interested in $[\pi^4 + \pi^2]$ cycloadditions, in which capto-dative ("c,d-") olefins play the role of the π^2 -component^{4,6-8)}.

On the other hand, the special design of the c,d-alkene 1 may enable the latter to act as 4e-component towards dienophiles. This is supported also by the following considerations: The two lowest energy bands in the He-I_α-photoelectron spectrum⁹⁾ of 1 at 9.07 eV and 10.25 eV have been assigned⁹⁾ to ionizations from the $(\pi_{CC} - \pi_s)$ - and $(\pi_{CC} + \pi_s)$ -orbitals, respectively. From its first I.P. alone, 1 should resemble an electron rich olefin like butylvinylether (1st I.P.: 9.08 eV¹⁰⁾) or methylvinylsulfide (8.45 eV¹¹⁾) rather than an electron poor olefin like acrylonitrile (10.91 eV¹⁰⁾). Cyclic thioenolethers do undergo [3+2]-cycloadditions to electron poor dienophiles to form unstable five membered cyclic sulfonium ylids¹²⁾.

When 19.4 mmoles of 1 were refluxed with 11.9 mmoles of N-phenyl maleic imide (2a) in 10 ml of purified dioxane for 5 days under argon, a 77% yield of a crystalline compound, m.p. 237 °C, could be isolated. Structure 4a (representing c-5-cyano-r-2,c-3-tetrahydrothiophenedicarboxylic



2-4 : a: X = N-C₆H₅; b: X = O

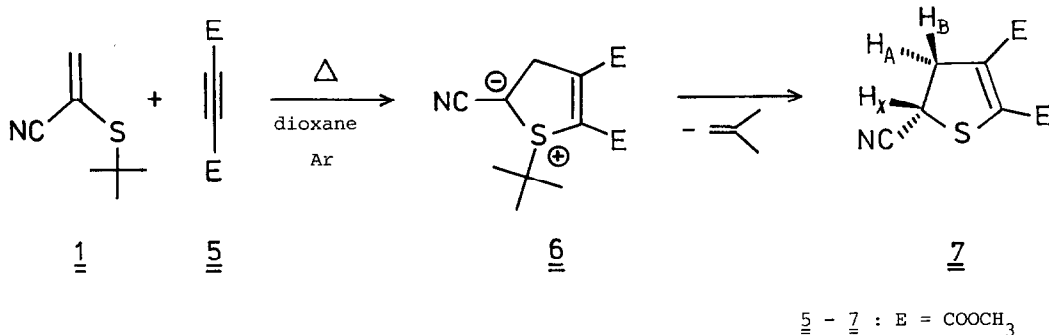
acid N-phenyl imide) was assigned to this compound on the basis of its elemental analysis and its spectral data. MS: $m/e = 260$ (4.6%, $M+2$); 258 (86%, M^+). - IR (KBr): 2230 cm^{-1} (CN). - $300\text{ MHz-}^1\text{H NMR}$ (acetone- d_6): Multiplets for one H each at δ 2.71 (ddd, exo-4-H), 3.11 (ddd, endo-4-H), 4.16 (ddd, 3-H), 4.60 (dd, 5-H), 4.72 (d, 2-H). The following coupling constants have been extracted: $^2J = -13.94\text{ Hz}$, $^3J_{4\text{-exo},3} = 8.84\text{ Hz}$, $^3J_{4\text{-endo},3} = 1.04\text{ Hz}$, $^3J_{4\text{-exo},5} = 6.86\text{ Hz}$, $^3J_{4\text{-endo},5} = 1.02\text{ Hz}$, $^3J_{2,3} = 8.14\text{ Hz}$.

From the reaction of 1 with maleic anhydride, under otherwise similar conditions, only a 19% yield of 4b could be obtained, m.p. $161\text{ }^\circ\text{C}$. - IR (KBr): 2238 cm^{-1} (CN), 1865 and 1795 (carboxylic anhydride). - $60\text{ MHz-}^1\text{H-NMR}$ (acetone- d_6): Signals for 1 H each at δ 2.75 (ddd, exo-4-H), 3.15 (ddd, endo-4-H), 4.45 (ddd, 3-H), 4.70 (dd, 5-H), 4.95 (d, 2-H), with the following coupling constants: $^2J = -14.8\text{ Hz}$, $^3J_{3,4\text{-exo}} = 8.5\text{ Hz}$, $^3J_{4\text{-exo},5} = 6.6\text{ Hz}$, $^3J_{4\text{-endo},5} = 1.7\text{ Hz}$, $^3J_{4\text{-endo},3} = 1.9\text{ Hz}$, $^3J_{2,3} = 8.6\text{ Hz}$. MS (70 eV): $m/e = 183$ (7%, M^+), 113 (4.6%) and 111 (100%, $\text{C}_5\text{H}_5\text{NS}$).

Formation of tarry by-products and the instability of the carboxylic anhydride moiety during chromatographic work-up impeded optimization.

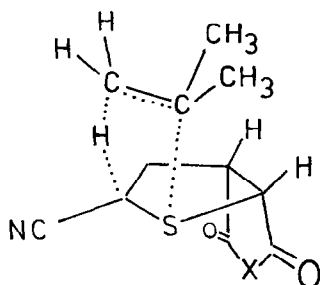
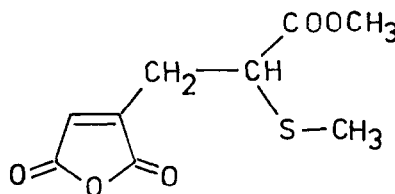
Under similar conditions as before, 1 (17 mmoles) also was added (with de-tert-butylation) to dimethyl ethyne dicarboxylate (5, 11 mmoles) to give an 84% yield of dimethyl 5-cyano-4,5-dihydrothiophene-2,3-dicarboxylate (7), m.p. $68\text{ }^\circ\text{C}$. - IR (KBr): 2240 (CN), 1730 and 1712 (CO, ester), 1620 (C=C). - MS (70 eV): $m/e = 229$ (2.5%, $M+2$), 227 (55%, M^+). - $60\text{ MHz-}^1\text{H NMR}$ (benzene- d_6): ABX $\delta_A = 2.83$, $\delta_B = 2.99$, $\delta_X = 3.73$, $J_{AB} = -17\text{ Hz}$, $J_{AX} = 11.2\text{ Hz}$, $J_{BX} = 3.3\text{ Hz}$; 3.42 and 3.48 (COOCH_3).

Successful additions have also been carried out²⁾ to norbornene (resulting in a mixture of diastereomers), 4-oxotricyclo[3.3.0.0^{2,8}]oct-6-ene-3-one¹⁴⁾ and cyclooctyne. Liberations of isobutene has been demonstrated by trapping it in a solution of bromine in carbon tetrachloride and identifying the resulting 1,2-dibromo-2-methylpropane by its IR spectrum¹⁵⁾.



Details of the course of this addition reaction of various c,d-olefins, its general scope and its limitations are currently under investigation²⁾. It is tempting to speculate, though, that the primary adduct is a cyano-stabilized ylide like 3a,b or 6, emanating from [3+2] cyclo-

addition of the electron rich olefin 1 to the electron poor dienophile. The conditions for ylide dealkylation are not as favourable as in the cases reported by Gollnick¹²⁾, however, (probably ionic) de-tert-butylations from sulfur in cyclic intermediates have been reported in other cases¹⁶⁾. The stereochemistry of 4a (the sole product isolated) as derived from the 300 MHz-¹H NMR spectrum is noteworthy and seems to suggest that the source of the proton attached to C-5 may well be the tert-butyl group itself, which, in the course of its elimination, donates the proton via a five membered cyclic transition state (8).

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It should be pointed out, that an analogue to 1, α -methylthioacrylic-acid methylester, has already been subjected to addition to maleic anhydride, and structure 9 had been assigned to the product¹⁷⁾.

The reaction reported here bears some analogy to the [3+2] cycloaddition of aryl aldehyde N-phenylhydrazones to maleic imides to yield pyrazoles reported recently¹⁸⁾ and employs also the combination of one CCS- and CC-fragment each to hydrothiophenes as does the thiophene synthesis from alkynethiolates and alkynes reported by Petrov and coworkers¹⁹⁾. It is the reversal of the fragmentation of 1-methylthiolanium iodide into ethylene and methyl vinyl sulfide under the influence of molar amounts of phenyl lithium²⁰⁾.

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