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DEPENDENCE OF TRANSMISSION OF CONJUGATION THROUGH CYCLOPROPANE RING INTO VINYL GROUP ON ELECTRON DEMAND OF SUBSTITUENT

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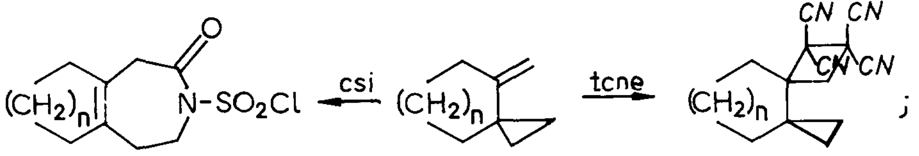
Summary. The placement of a methoxycarbonyl or a cyano group on the cyclopropane ring in *spiro*-vinylcyclopropanes (7a, 7b) causes a drain of electrons from the vinyl group through the ring into the electron demanding substituent, precluding their [2+2]cycloaddition with TCNE but not with the stronger electrophilic olefin CSI (7 → 8), whereas the placement of a hydroxymethyl group renders the vinyl group reactive toward TCNE (9 → 13).

In continuation of our studies of the cycloadditions between electron-rich homodienes of the *spiro*-vinylcyclopropane structure (1) and electron-deficient olefins we became interested in effects of substitution on the two distinctly different modes of cycloaddition: (i) the [2+2] cycloaddition of tetracyanoethylene (TCNE) (1 → 2)[1], and (ii) the [2+5] cycloaddition of N-chlorosulfonylisocyanate (CSI) (1 → 3).[2]



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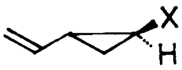

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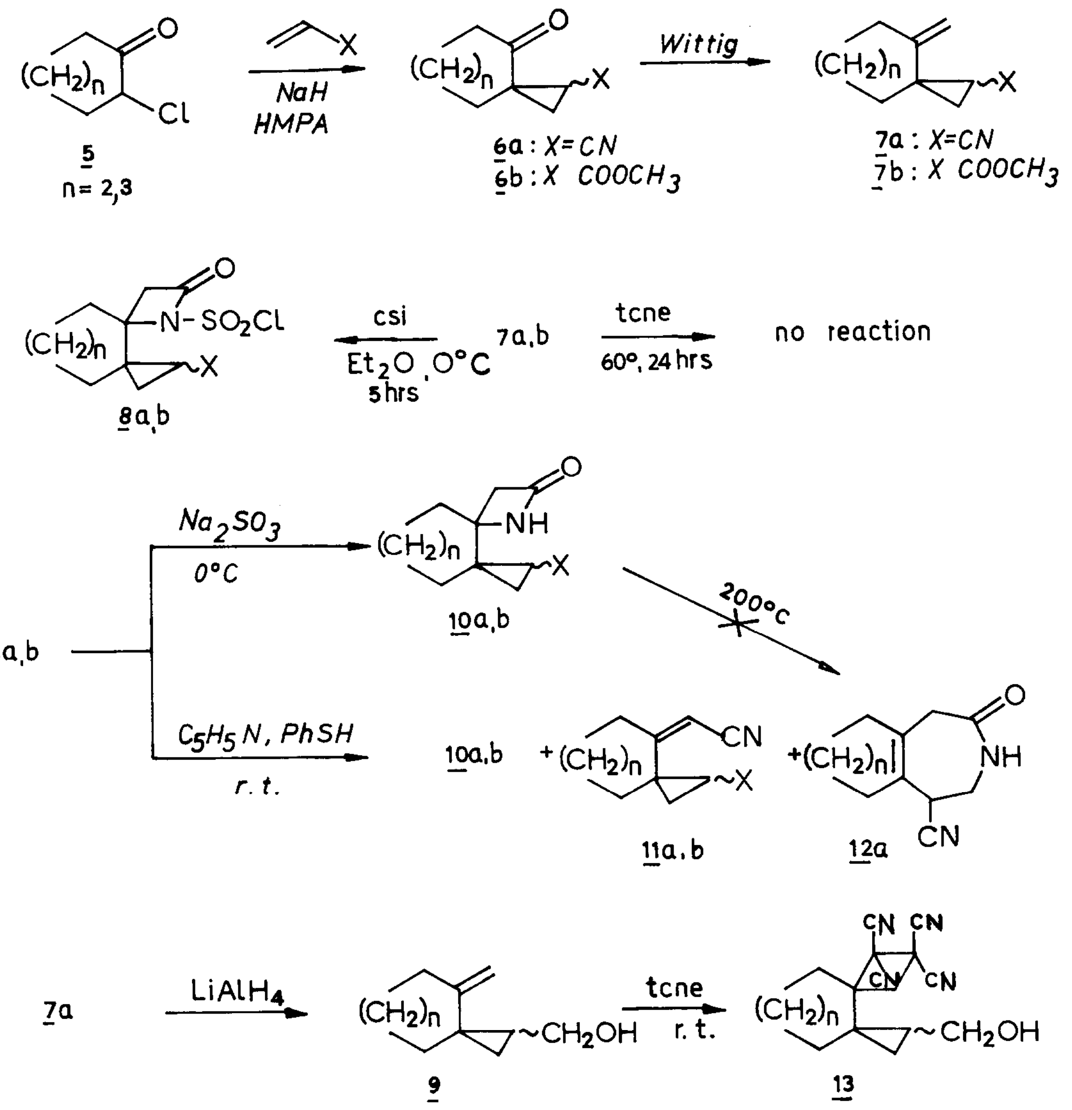
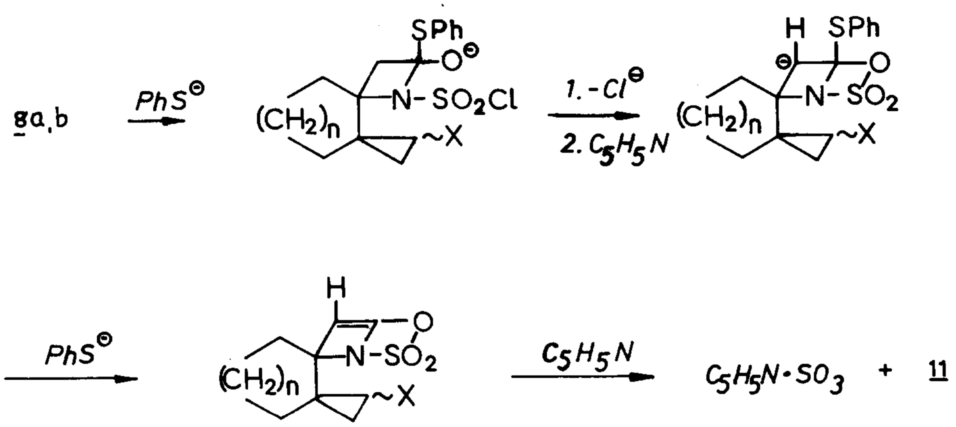
From semiempirical calculations (INDO method) on a series of *trans*-2-vinylcyclopropylcarbinyl derivatives (4) Kispert, et al.[3] concluded that "transmission of conjugation from carbinyl group through the ring into the vinyl group is either small or nonexistent". The only exception is the case where X = CH_2^+ .

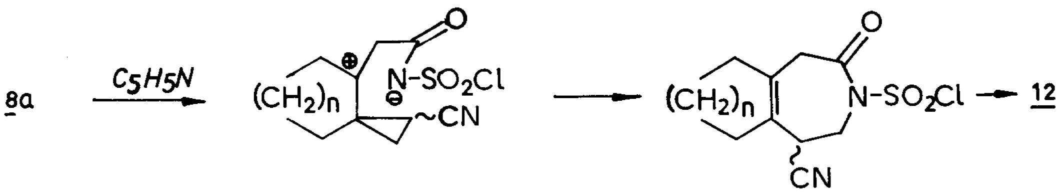
This communication describes the chemical consequences resulting from placement of substituents of high electron demand on the cyclopropane ring in *spiro*-vinylcyclopropanes on the reactivity of the vinyl group toward electrophilic olefins. We found that introduction of CN or $COOCH_3$ on the small ring renders the vinyl group in (7) unreactive to TCNE even at 60°C, but quite reactive to CSI at 0°C to provide the corresponding β-lactams (8). The reactivity of the double-bond toward TCNE changed dramatically on converting the carboxylic ester (7b) into the electron-releasing hydroxymethyl group (9). The latter underwent a facile [2+2] cycloaddition to yield (13).



The 1-cyano- and 1-methoxycarbonyl-4-methylene-*spiro*[2.5]octane and *spiro*[2.6]nonane (7a,b, n=2,3)[4] failed to react with TCNE even after 24 hrs. of exposure. By contrast, the exposure of 10 mmoles of (9) to the action of TCNE (12 mmoles) in CH_3CN solutions at room temperature for 24 hrs. provided 42% crystalline adducts melting at 121-123°C (9, n=2) and at 117-119°C (11, n=3). When 20 mmoles of (7a,b) in 30 ml of dry ether were allowed to react at 0°C, under N_2 atmosphere, with CSI (25 mmoles in 10 ml dry ether) until the typical IR bands for CSI at 2240 and 2260 cm^{-1} disappear, solid adducts, strongly hygroscopic of structure (8a,b) were collected and characterized; (8a, n=3), m.p. 110-112°C; IR (NaCl): 2240s (CN), 1810s (C=O) cm^{-1}; ^{1}H-nmr (60 MHz, $CDCl_3$): 8.78 τ (s, 2H) and 7.62 (1H, bs, cyclopropane), 6.73 (2H, s, β-lactam).

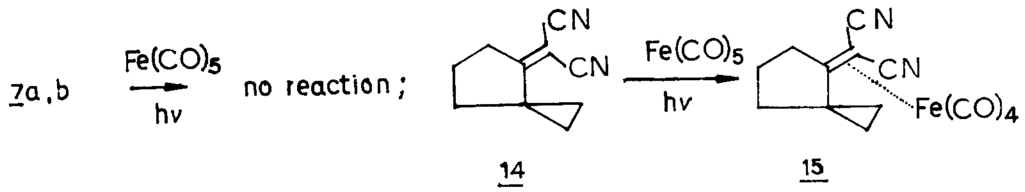
The N-chlorosulfonyl group in adducts (8a,b, n=2,3) was reduced in two ways: by the Na_2SO_3[6] method and by the thiophenol-pyridine method.[7] The first one provided (10) as the sole isolable product in ca. 65% yield. Significantly, the second one provided a 8:1:1-mixture of (10), (11) and (12) in overall yield of ca. 70%, implying that thiophenol plays an active role in generation of the two minor products as delineated below.





On gas chromatography (6¼ column, 20% carbowax 20M, 200°C, 40 ml. He/min.) 10a,(n=3) had R_t 32.7 min.; 11a (n=3): 17.8 min., m.p. 150-152°, and 12a (n=3): 52.0 min. In the IR (NaCl) region 10a (n=3) exhibited bands (cm^{-1}) at 3270s (NH) and 1745s (C=O); 11a (n=3) : 1605 s (C=C); 12a (n=3) : 3520 m (NH), 1780s (C=O), 1605 m (C=C). The elementary analysis ^1H-nmr (60 MHz) and mass spectra of all CSI adducts and derivatives are in conformity with the structures assigned. Compound 10a (n=3) could not be converted on heating at 200° into 12a (n=3), implying that the 7-membered lactam was formed at an earlier stage of the reaction.

The σ,π-electron system in (7) manifest high sensitivity to substitution effects. The cyclopropane ring is evidently able to trasmit effectively conjugation from the polar subsituent through the ring into the vinyl group. An extra dimmension is added in this context to the inclusion of the $Fe(CO)_5$-induced photolysis to a series of (7) in which X equals H, CN and $COOCH_3$ and to a 4-dicyanomethylene-*spiro*[2.x]alkanes (14). Study has shown that whereas (7, X=H) reacts smoothly with $Fe(CO)_5$ to provide high yields of carbonyl insertion products,[8] (7a) and (7b) were recovered unchanged from the reaction mixture. Significantly, the photolysis of (14) provided the tetracarbonyliron π-complex (15) in which the small ring remarkably resists an attack by the transition metal.[9]



The displacement of CO from $Fe(CO)_5$ appears to depend both on the electron donor capacity of the cyclopropane ring in the σ,π-system (7a) and on the electrophilicity of the metal.[10]

REFERENCES AND FOOTNOTES

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4. 1-cyano-4-methylene-*spiro*[2.5]octane, 7a, n=2, b.p. 38-42°/0.01 mm; 1-cyano-4-methylene-*spiro*[2.6]nonane, 7a, n=3, b.p. 72-74°/0.01 mm; 1-methoxycarbonyl-4-methylene-*spiro*[2.5]-octane, 7b, n=2, b.p. 55-56°/0.02 mm; 1-methoxycarbonyl-4-methylene-*spiro*[2.6]nonane, 7b, n=3, b.p. 58-62°/0.01 mm, were obtained through Wittig reaction of respective ketones (6a,b, n=2,3) which, in turn, resulted from the sodium hydride-catalysed condensation of the corresponding α-chloroketones (5, n=2,3) with acrylonitrile and methyl acrylate, respectively, following the procedure as described.[5]
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