

NOVEL SYNTHESIS OF HETEROCYCLIC SPIRANS
BY TANDEM CYCLOADDITION TO SULFUR-CONTAINING HETEROCUMULENES

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Summary: Novel Ni(CO)₄-promoted tandem cycloadditions of diphenylcyclopropenone to isothiocyanates and to CS₂ were found to provide new heterocyclic spirans, pyrroline-2-one-5-spiro-5'-thiolene-4'-ones and a thiolene-2-one-5-spiro-5'-thiolene-4'-one, respectively, in moderate yields.

Cycloadditions of heterocumulenes are of extensive use in heterocyclic synthesis. However, tandem cycloaddition to the cumulative bonds leading to heterocyclic spirans has been less known. On the other hand, synthetic application of metal carbonyls to heterocyclic synthesis has been of great interest because of an increase in reactivity and selectivity and/or of direct incorporation of carbonyl moiety.¹ Combining these two reagents, we have reported several new types of heterocyclic syntheses.² Recently, we found that the reaction of diphenylcyclopropenone with an isothiocyanate or with carbon disulfide gives a 2:1 cycloadduct (tandem adduct) as well as a 1:1 adduct in the presence of tetracarbonyl nickel. Tandem addition to isothiocyanates has not been known in spite of some reports on that to carbon disulfide.³ Thus the new spirans (2:1 adducts) obtained are featured as a result of a metal carbonyl-promoted tandem cycloaddition to the heterocumulenes.



Equimolar amounts of the isothiocyanate **1**, diphenylcyclopropenone (**2**), and Ni(CO)₄ were reacted in DMF at 65-70°C to give the two heterocyclic spirans **4** and **5** in addition to the pyrroline **3**. The results are listed in Table 1. The use of two moles of the propenone **2** unexpectedly gave a lower yield of **4a**. While benzoyl isothiocyanate (**1b**) gave only the adduct **4b** in a better yield, the alkyl isothiocyanate **1c** gave no adduct. Although the 2:1 adduct **4a** seems to be formed via the 1:1 adduct **3a**, the isolated **3a** did not react with **2** in the

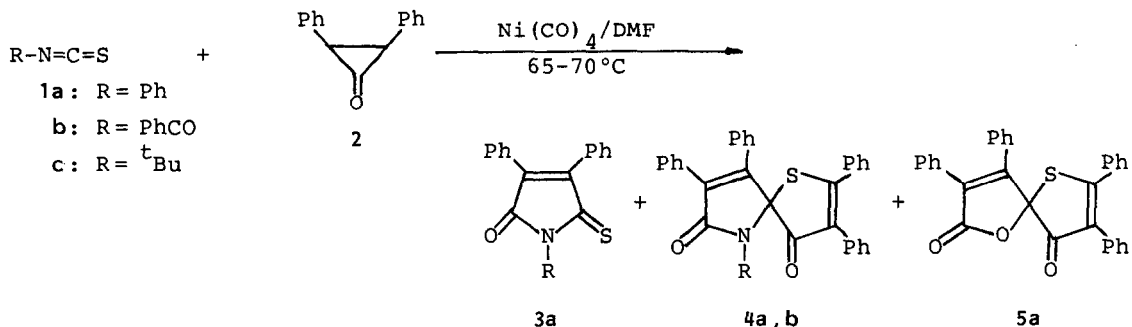
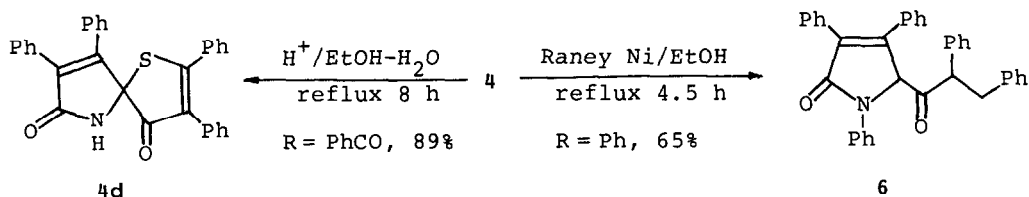


Table 1. Reaction of the Isothiocyanates 1 with the Propenone 2.

Isothiocyanate 1		Mole Ratio			Reaction	Yield (%)		
R		1 : 2 : Ni(CO) ₄			Time (h)	3	4	5
1a	Ph	1	1	1	7	6	30	17
1a	Ph	1	1	0.5	7	6	9	7
1a	Ph	1	2	1	5	trace	17	16
1b	PhCO	1	1	1	4	-	55	-
1c	<i>t</i> -Bu	1	1	1	4	-	-	-

presence of Ni(CO)₄ at 70°C. The structures of the products 3-5 were determined by spectral and analytical data as well as by chemical evidence.^{4,5} Among them the ¹³C nmr spectra of 4a showed a singlet of the spiro carbon at 84.2 ppm and the two types of carbonyl carbons at 171.7 (CO-N) and 196.1 ppm (CO-C=C). Desulfurization of 4a with Raney nickel afforded the pyrroline 6.



The structure of 4a was unambiguously established by a single-crystal X-ray analysis. *Crystal data:* C₃₇H₂₅NO₂S, M 547.7, monoclinic, space group $P2_1/c$, $a = 20.810(2)$, $b = 16.000(1)$, $c = 18.131(1)$ Å, $\beta = 107.77(1)^\circ$, $V = 5748.7(6)$ Å³, $D_c = 1.266$ g cm⁻³ for $Z = 8$, $\mu(Cu\ K\alpha) = 12.3$ cm⁻¹. The intensity data were collected by the θ - 2θ scan technique on a Rigaku automated four-circle diffractometer using Nickel-filtered Cu K α radiation. The structure was solved by the direct method (MULTAN),⁶ and refined including all H atoms by the block-diagonal least-square procedure (HBL5 V):⁷ $R = 0.062$ for 4609 observed reflections ($|F_o| > 3\sigma(|F_o|)$).⁸ The spiran skeletons in two crystallographically independent molecules in a symmetric unit are not different from each other

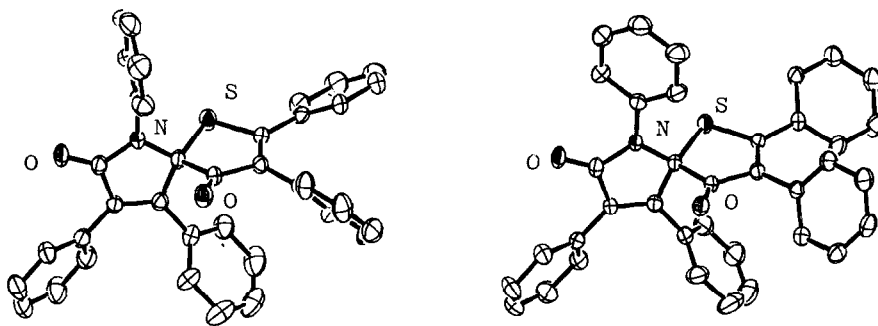
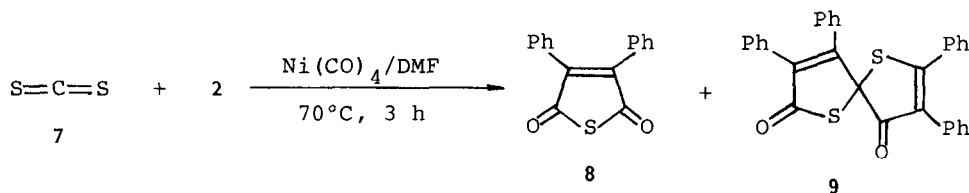


Fig 1. Two crystallographically independent molecules of 4a (ORTEP⁹ drawing).

The spiran skeletons in these molecules have the same structure, however, four benzene rings out of five take different conformations to the spiran rings to which they attached.

(Figure 1), and these structures are consistent with that assigned by the spectral data.

Carbon disulfide, similarly, reacted with the cyclopropenone 2 to give the tandem cycloadduct 9 along with a small amount of the 1:1 cycloadduct 8 and the results are summarized in Table 2. The yield of the spiran 9 was higher when the reaction was carried out in a sealed tube. But an increase or a decrease in the amount of $\text{Ni}(\text{CO})_4$ did not cause positive effect. The ^{13}C nmr spectra of 9 was very informative: a singlet at 72 ppm showed the presence of a spiro



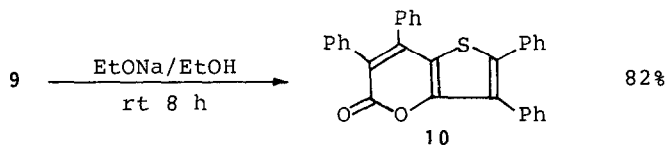
carbon and two singlets of CO carbons at 195.6 and 195.7 ppm suggested its unsymmetrical structure. It is quite interesting that the tandem addition of 2 to carbon disulfide did not give a symmetrical adduct, which has been the case with the known tandem additions.³

The structure of the maleic thioanhydride 8 was determined by spectral and analytical data, where ^{13}C nmr data clearly showed its symmetrical structure.⁵ Treatment of the spiran 9 with sodium ethoxide in ethanol gave the thieno-

Table 2. Reaction of Carbon Disulfide 7 with the Cyclopropenone 2.

Mole Ratio			Yield (%)	
7	2	$\text{Ni}(\text{CO})_4$	8	9
1	1	1 ^{a)}	3	21
1	1	1 ^{a)}	3	41 ^{b)}
1	2	1 ^{a)}	trace	43
1	2	1 ^{a)}	6	42 ^{c)}
1	2	3	trace	32
2	1	0.5	3	20

a) In a sealed tube. b) The compound 10 was obtained (4%).
c) 10 was obtained (5%).



pyrone derivative 10, which was isolated as a byproduct in some runs (see Table 2). The pyrone was also obtained by treating 9 with Raney nickel in THF (41%). The structure of 10 was well established by the spectral data.⁵

The formation of the above new heterocyclic spirans is assumed to be affected by a nickelacyclobutenone intermediate, since the cyclopropenone is unreactive to heterocumulenes without metal carbonyls.² However, mechanistic studies as well as further details in this type of reactions are in progress.

REFERENCES AND NOTES

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- 4) The pyrroline 3a was oxidized with MCPBA to give 1,3,4-triphenylpyrroline-2,5-dione (65%), which was identified with an authentic sample and reduced with Raney nickel to give 1,3,4-triphenyl-(5H)-pyrroline-2-one (92%); mp 189-190°C (pale yellow needles); ir (Nujol) 1690 cm⁻¹ (C=O); ¹H-nmr (CDCl₃) δ 4.73 (s, 2H, CH₂), 7.10-8.00 (m, 15H, Ph); MS m/e 311 (M⁺); e.a. ±0.17%.
- 5) Key spectral data for the main compounds are as follows: 3a; mp 163-164°C (yellow needles); ir (Nujol) 1690 cm⁻¹ (C=O); MS m/e 341 (M⁺); mp 198-199°C (yellow prisms); ir (Nujol) 1700 and 1690 cm⁻¹ (C=O); ¹³C-nmr (CDCl₃) 84.2 (>C<), 149.7 (NCOC=C), 169.8 (COC=CS), 171.7 (NC=O), 196.1 ppm (C=O); MS m/e 547 (M⁺); 5a; mp 203-204°C (pale yellow needles); ir (Nujol) 1780 and 1700 cm⁻¹ (C=O); ¹³C-nmr (CDCl₃) 94.3 (>C<), 155.8 (OCOC=C), 170.3 (COC=CS), 171.1 (OC=O), 194.1 ppm (C=O); MS m/e 472 (M⁺); 8; mp 151-152°C (yellow needles); ir (Nujol) 1705 and 1680 cm⁻¹ (C=O); ¹³C-nmr (CDCl₃) 148.5 (C=C), 191.4 ppm (C=O); MS m/e 266 (M⁺); 9; mp 200-201°C (yellow needles); ir (Nujol) 1710 and 1690 cm⁻¹ (C=O); ¹³C-nmr (CDCl₃) 72.0 (>C<), 160.4 (SCOC=C), 171.6 (COC=CS), 195.6 (C=O), 195.7 ppm (C=O); MS m/e 488 (M⁺); 10; mp 288-289°C (yellow needles); ir (Nujol) 1700 cm⁻¹ (C=O); ¹³C-nmr (CDCl₃) 119.4 and 121.2 (OC=CS and SC=C), 143.8 (COC=C), 148.2 (COC=C), 152.3 (OC=C), 162.3 ppm (OC=O); MS m/e 456 (M⁺). Elemental analyses of the compounds were satisfactory within an error of ±0.39%.
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- 8) The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.
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(Received in Japan 16 March 1985)