$^3J$(H-H) ≈ 7.0, 1 H), 7.42 (d, $^3J$(H-H) ≈ 7.8, 1 H), 7.70 (t, $^3J$(H-H) = 7.6, 1 H), 9.00 (dd, $^3J$(H-H) = 5.6, $J$ = 1.3, 1 H); mass spectrum ($^{96}$Mo), $m/z$ 535 (M, 19); IR (toluene) $\nu$ (CO) 2010 (m), 1890 (vs), 1855 (vs). Anal. Calcd for $C_{25}H_{30}NO_4PMo$: C, 56.10; H, 5.61. Found: C, 55.88; H, 5.62.

**Decomplexation of the Mo(CO)$_4$ Complex 16.** Complex **16** (1 mmol) and diphos (1 mmol) were heated at 100 °C for 2.5 h in toluene (5 mL) under argon. After evaporation and extraction with pentane, the phosphine **17** was purified by filtration through a short Celite column. **17**: yield 0.26 g (80%), colorless oil; $^{31}$P NMR ($C_6D_6$) $\delta$ 9.06; $^1$H NMR ($C_6D_6$) (400 MHz) $\delta$ 0.77 (d, $^3J$(H-H) = 6.7, $CH_3$), 0.81 (d, $^3J$(H-H) = 6.7, $CH_3$), 0.89 (d, $^3J$(H-H) = 6.3, $CH_3$), 1.0-1.9 (m), 2.48 (t, $J$(H-H) ≈ $J$(H-P) = 8.9, 1 H), 2.86 (d, $J$ = 3.07, 1 H), 3.09 (s, 1 H), 3.23 (d, $J$(H-P) = 25.3, 1 H), 6.0-6.1 (m, 2 H, CH=CH), 6.61 (t, $^3J$(H-H) ≈ 6.1, 1 H), 7.10 (t, $^3J$(H-H) ≈ 6.7, 1 H), 7.29 (d, $^3J$(H-H) = 7.8, 1 H), 8.51 (d, $^3J$(H-H) = 4.8, 1 H); mass spectrum, $m/z$ 327 (M, 17), 188 (M - Men, 100).

**X-ray Structure Determinations.** Single crystals of both compounds were grown at 4 °C from hexane solutions. Data were collected at 20 ± 1 °C on an Enraf Nonius CAD4 diffractometer; Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å) and a graphite monochromator were used. The crystal structures were solved and refined using the Enraf Nonius supplied SDP package. Direct methods provided a suitable starting point, and the initial model was obtained from difference Fourier maps. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms.

Compound **8b**: $C_{26}H_{35}O_5PW$ crystallises in space group $P6_5$, $a$ = 10.998 (1) Å, $c$ = 40.064 (4) Å; $V$ = 4195.47 (2.48) Å$^3$; $Z$ = 6; $d_{calcd}$ = 1.525 g/cm$^3$; $\mu$ = 43.0 cm$^{-1}$; $F$(000) = 1920. A total of 4175 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$ of which 2326 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 1849 for solution and refinement. A non-Poisson weighting scheme was applied with a $p$ factor equal to 0.08. The final agreement factors were $R$ = 0.037, $R_w$ = 0.056, G.O.F. = 1.11. For the enantiomeric space group, these factors were respectively equal to 0.042, 0.062, and 1.22.

Compound **13**: $C_{27}H_{32}NO_5PW$ crystallises in space group $P2_1$, $a$ = 11.352 (1) Å, $b$ = 14.419 (1) Å; $c$ = 17.007 (2) Å, $\beta$ = 94.30 (1)°; $V$ = 2775.95 (79) Å$^3$; $Z$ = 4; $d_{calcd}$ = 1.592 g/cm$^3$; $\mu$ = 43.4 cm$^{-1}$; $F$(000) = 1320. A total of 8356 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$; 5299 of these were considered as observed and used for structure solution and refinement. A non-Poisson weighting scheme was applied with a $p$ factor equal to 0.06. The final agreement factors were $R$ = 0.031, $R_w$ = 0.039, G.O.F. = 1.00. For the enantiomeric structure, these factors were respectively equal to 0.048, 0.068, and 1.754.

**Acknowledgment.** We thank Elf-Aquitaine-Groupement de Recherches de Lacq for financial support and Dr. Jean-Alex Laffitte for fruitful discussions.

**Supplementary Material Available:** Tables of crystallographic data, positional and displacement parameters, and bond distances and angles (15 pages); tables of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

# Can Polymerization Trap Intermediates in 1,3-Dipolar Cycloadditions?

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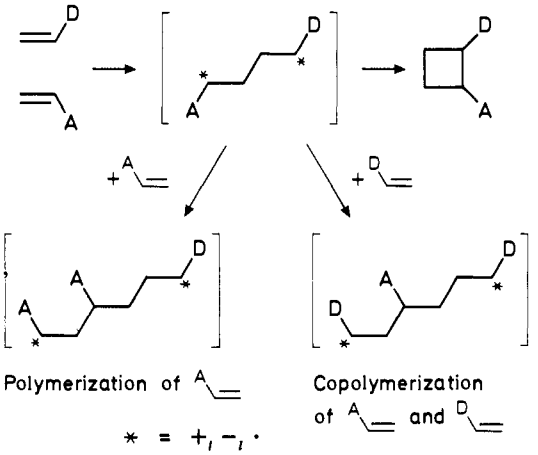
**Abstract:** 2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-methylide (TTCM) is a nucleophilic 1,3-dipole which is known to undergo two-step cycloadditions to very electron poor olefins. When this 1,3-dipole is generated from its precursor, the 1,3,4-thiadiazoline **7**, in acrylonitrile or acrylic esters at 45 °C, only cycloaddition and no polymerization is observed, suggesting a concerted cycloaddition. Small amounts of polymers were observed alongside the cycloadducts with nitroethylene, methacrylonitrile, and methacrylates. Most cycloadducts were produced as regioisomeric mixtures. The reaction of TTCM with benzylidenemalononitrile, a nonpolymerizable olefin, is nonconcerted and furnished in THF and 1 vol % methanol or 3 vol % water a 7-membered lactim methyl ether or lactam formed by interception of a ketene imine. The observed polymerizations are radical in nature and are proposed to be initiated by a minor contribution of a diradical intermediate to the cycloaddition reaction.

## Introduction

The evidence for the concerted character of certain cycloadditions is necessarily *indirect* and centers on the exclusion of intermediates.[2] The experimental criteria for diradical or zwitterionic intermediates are based on the phenomena of *kinetic competition*.[3] The interception of a putative intermediate must be competitive in rate to its ring closure. Nonstereospecificity is observed when bond rotation in the intermediate successfully competes with the generally very rapid ring closure. Rate measurements can also speak in favor of or against concertedness. Sometimes substituent effects on the rate allow one to distinguish between early, i.e., reactant-like transition states, and late ones, which are structurally close to intermediates.[4] The dependence of rate on solvent polarity is informative about the amount of charge separation in the activation process.

**Scheme I**




(1) (a) Universität München. (b) University of Arizona. (c) On leave from the University of Lodz, Poland.
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The main experimental problem with trapping experiments is the necessity to find a reagent which combines sufficiently fast with the intermediate. A few years ago, the Tucson group introduced a new system of intercepting an intermediate in a cycloaddition:[5] this technique is based on the use of a polymerizable compound as the trapping agent (Scheme I). If either of the two arms of the intermediate adds to the polymerizable compound, a chain polymerization is started. The intermediate thus acts as an initiator of polymerization, with its other arm bearing the counterion or another radical.

The main advantage of this technique is its sensitivity: one molecule of the intermediate will give a polymer with a molecular weight that can be hundreds of times larger than that of a molecule resulting from the trapping of the same intermediate with a small molecule. This means that even if the monomer chosen for interception can only trap a small proportion of all of the formed intermediates, the resulting polymer will be formed in an isolable quantity. An advantage of the method is that it is intrinsically easy to separate a polymer from low-molecular-weight products and to identify it. These ideas were shown to be very efficient in the investigation of [2 + 2] cycloadditions. In polymer chemistry, they also explained why polymers form spontaneously when some monomers are mixed in the absence of initiator (the "Bond-Forming Initiation" theory).[5,6] We were interested to test the applicability of this concept to other types of cycloadditions, especially in cases where the nonconcerted character had been demonstrated earlier.

Normal 1,3-dipolar cycloadditions fulfill all of the criteria of concertedness.[7] The recent observation of two-step 1,3-dipolar cycloadditions via zwitterionic intermediates by the Munich group[8,9] was guided by an FMO concept: strong predominance of the HO(1,3-dipole)–LU(dipolarophile) interaction and steric hindrance at one terminus promote the "one-bond mechanism".[10] Due to the absence of electronegative key atoms, thiocarbonyl ylides have high HO energies and their cycloadditions to very electrophilic olefins proceed via zwitterions.

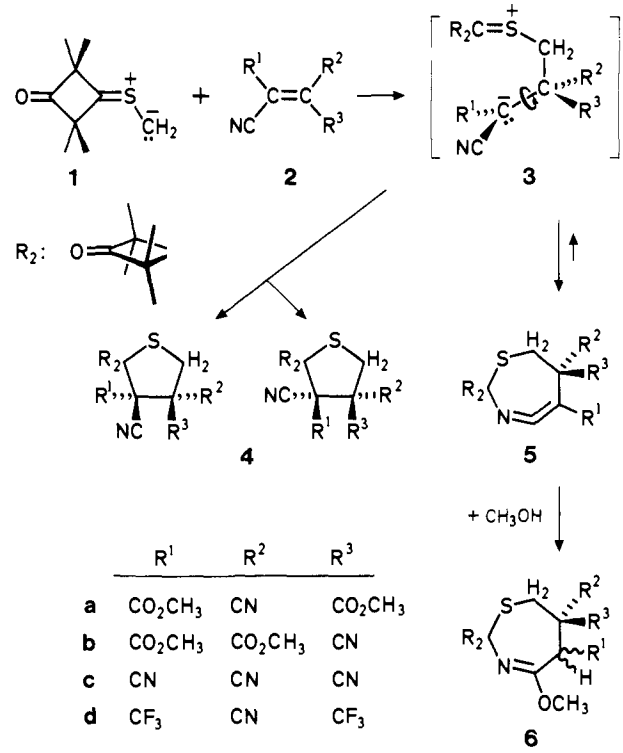
Recently, Quast et al. isolated zwitterions arising from the reaction of highly electrophilic azides with 5-alkylidenedihydrotetrazoles;[11] they established that these zwitterions were real intermediates in the cycloadditions and were not derived from a blind-alley equilibrium. Among the FMO interactions, the one of LU(1,3-dipole) with HO(dipolarophile) is strongly predominant in this case.

On the basis of these few observations of nonconcerted behavior involving 1,3-dipoles, the reactions of a thiocarbonyl ylide with electrophilic olefins were reinvestigated. In the literature, we found no example of a polymerization directly initiated by a 1,3-dipole, and some 1,3-dipoles are even known to inhibit free radical polymerization.[12] The trapping by polymerization concept was applied to the reactions of 1,3-dipoles with, or in the presence of, polymerizable olefins.

## Results and Discussion

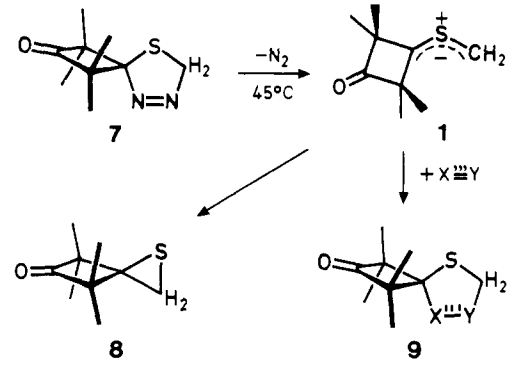
**Reactions of 2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-Methylide: Background.** The 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methylide (TTCM, **1**) is a 1,3-dipole with one sterically screened terminal C-atom. Substantial stereochemical leakage occurs during the cycloadditions of TTCM to dimethyl

Scheme II




| | R¹ | R² | R³ |
|---|---|---|---|
| a | $CO_2CH_3$ | CN | $CO_2CH_3$ |
| b | $CO_2CH_3$ | $CO_2CH_3$ | CN |
| c | CN | CN | CN |
| d | $CF_3$ | CN | $CF_3$ |

Scheme III




2,3-dicyanofumarate and dimethyl 2,3-dicyanomaleate (**2a,2b**), furnishing mixtures of thiolanes **4** (Scheme II).[8,13] Whereas TTCM combines with tetracyanoethylene in absolute THF to give **4c**, the presence of 0.6–6% methanol in the solvent gives rise to the lactim methyl ether **6c** in a 65:35 ratio alongside thiolane **4c**. The ketene imine **5c** was postulated as an intermediate, the result of intramolecular trapping of zwitterion **3c**. With 1,2-bis(trifluoromethyl)ethylene-1,2-dicarbonitrile (**2d**), the ketene imine **5d** is isolable and is the first known 7-membered cyclic ketene imine;[14] on heating, **5d** isomerizes to the thiolane **4d** via **3d**.[15] The structure of a related crystalline ketene imine was confirmed by X-ray.[16]

TTCM is generated by the thermal 1,3-dipolar cycloreversion of the 1,3,4-thiadiazoline **7**,[17] the 1,3-cycloadduct of diazomethane to the thione. The half-life of **7** amounts to 25 min in xylene at 45 °C[18] and is independent of the nature of the dipolarophile. TTCM is not a stable 1,3-dipole; in the absence of a reactive partner, it rapidly affords the thiirane **8** by electrocyclization.[17]

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Table I. Reaction of TTCM with Polymerizable Olefins[a]

| entry | olefins | cycloadduct % yield | regioisomeric ratio **10**/**11** | % thiirane **8** | % polymer conversion |
|---|---|---|---|---|---|
| a | acrylonitrile | 79 | 4.0 | 0 | 0 |
| b | methyl acrylate | 96 | 2.5 | 0 | 0 |
| c | *tert*-butyl acrylate | 97 | 0.3 | 0 | trace |
| d | nitroethylene | | only **10** | 0 | 1.4–2.8 |
| e | methacrylonitrile | 36 | 1.0 | 57 | 0.2 |
| f | methyl methacrylate | 40 | 0.4 | 35 | 2.6 |
| g | *tert*-butyl methacrylate | 23 | only **11** | 12 | 3.6 |

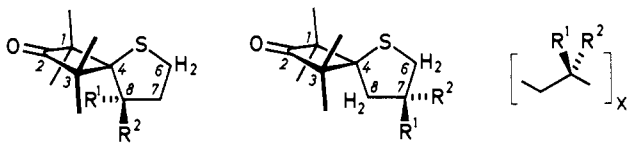
[a] Reaction conditions: $3 \times 10^{-4}$ mol of **7** + 2 mL of olefin, 8 h, 45 °C.

So far TTCM has not been spectroscopically characterized (Scheme III).

Due to high HO energies, thiocarbonyl ylides are very nucleophilic 1,3-dipoles. In a first survey by the Munich group,[18] TTCM combined in situ with ethylenes and acetylenes, most of which were 1,2-disubstituted by electron-withdrawing groups, furnishing cycloadducts **9** in 72–93% yields. Thiones are "superdipolarophiles".[19] TTCM reacted with thiobenzophenone and thioxanthione yielding regioisomeric cycloadducts, whereas sterically hindered aliphatic thiones such as adamantanethione gave rise only to **9** (X = S). β-Nitrostyrene and chloral afforded the adducts expected for a nucleophilic $CH_2$ terminus.[18]

**Reactions of TTCM with Polymerizable Olefins.** The idea that zwitterionic intermediates corresponding to **3** might be good initiators of anionic chain polymerization was the starting premise of this work; the counterion would be stabilized by the adjacent thioether group and the bulkiness of the tetramethylcyclobutanone ring would prevent rapid termination. To test the reactivity of TTCM as an initiator of polymerization, we studied its reactions with various polymerizable olefins. In each case, **7** was dissolved in an excess of the pure olefin and heated under argon to 45 °C. Such conditions have adverse effects on anionic polymerizations; the temperature is unusually high and is expected to favor classical side reactions during the propagation.[20] Unfortunately, this temperature is necessary for **7** to generate TTCM at a reasonable rate. On the other hand, the use of the olefin as the solvent of the reaction should allow for efficient trapping of the intermediate. The results of the reactions of **7** with polymerizable olefins are summarized in Table I.

In our study, we were mainly restricted to the use of monosubstituted and 2,2-disubstituted olefins. Acrylonitrile and methyl acrylate gave no polymer but high yields of the thiolanes **10a**,**b** and **11a**,**b**. This behavior is compatible with a concerted cycloaddition of TTCM. Correspondingly, the Munich group reported that fumaronitrile, maleonitrile, and dimethyl fumarate react stereospecifically (>99.95%) with TTCM.[8,21] Apparently, one or two electron-withdrawing substituents do not lower the energy of LU(dipolarophile) sufficiently for the two-step process to take control. The slower cycloaddition to dimethyl maleate gave rise to *cis*- and *trans*-thiolane in a 99:1 ratio,[8] suggesting a minor participation of the stepwise pathway.




The presence of two regioisomers in the reactions with acrylonitrile and methyl acrylate offers the first examples of monosubstituted ethylenes as dipolarophiles that do not exclusively yield the expected isomer **10** with TTCM. By crystallization of the methyl acrylate product from methanol and pentane, the thiolanes **10b** and **11b** were separated and obtained in pure form. The path to the thiolane **10** with a substituent at C8 is sterically more demanding but probably electronically favored by a larger atomic orbital coefficient at the $CH_2$ terminus of TTCM. The influence of steric factors became clear by replacing methyl acrylate with *tert*-butyl acrylate; **11c** was then the favored product.

Adding a methyl group to the α-position of the monosubstituted olefin has the same effect on the regioselectivity. *tert*-Butyl methacrylate, for which only **11g** was detected, constitutes an extreme. Obviously, the increasing bulk of the olefin in the transition state leading to **10** results in serious steric interactions between the ethylenic substituents and the *gem*-dimethyl groups on the side of TTCM.

Nitroethylene also gave a significant amount of polymer. Although a blank did not produce poly(nitroethylene), the origin of this polymerization is in doubt. Indeed, the conversion of nitroethylene into its polymer was found to vary from one experiment to another (1.4–2.8%). Nitroethylene is known to rapidly polymerize in the presence of water.[22,23] We found that the addition of 2 vol % water to nitroethylene is sufficient to cause rapid polymerization; under the same practical conditions as used during the reaction with **7**, a 8.8% conversion was obtained. Thus, we cannot exclude a trace of water being responsible for the observed polymerization. 2-Nitropropene was investigated, but it spontaneously decomposed under the experimental conditions. Its thermal instability had been reported earlier.[23]

Remarkably, the cycloaddition to nitroethylene obeyed the electronically favored orientation and afforded only **10**. According to Charton's scale of steric demands,[24] a nitro group is not very different from an ester or a nitrile function. The disparity may be linked to the higher electron attraction by the nitro group; nitroethylene possesses a larger AO coefficient in the LU at the β-position than the other acceptor olefins.

The concerted mechanism is more sensitive to steric factors than the two-step pathway. Accordingly, with the increase of steric hindrance the production of polymers rose, despite the known reduced polymerizability of bulkier olefins. *tert*-Butyl acrylate was found to form trace amounts of poly(*tert*-butyl acrylate); the quantity was too low to be isolated by precipitation, but the polymer was clearly present in the 500-MHz $^1H$ and $^{13}C$ NMR spectra of the crude reaction mixture. No polymer formed when *tert*-butyl acrylate was subjected to the same experimental conditions in the absence of **7**. Methyl methacrylate, *tert*-butyl methacrylate, and methacrylonitrile all gave reproducible amounts of their corresponding polymers. Reactions with methyl methacrylate run in the presence of inhibitors proved that the polymerization was radical in nature; *p*-toluenesulfonic acid and trifluoroacetic acid did not inhibit the polymerization, but TEMPO (2,2,6,6-tetramethylpiperidinoxyl free radical) and DPPH (2,2-bis(4-*tert*-butylphenyl)-1-picrylhydrazyl free radical), two known inhibitors of radical polymerization, suppressed the polymerization completely.

The added methyl group in the methacrylic esters influenced the regioselectivity and promoted polymerization. Both phenomena reflect the decreased overall rate of TTCM interaction with these acceptor olefins. Substantial amounts of thiirane **8** testify to the now successfully competing electrocyclization. The

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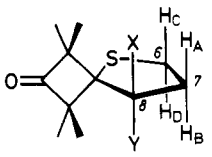
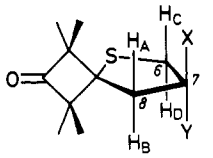
Table II. $^1$H NMR Data for Cycloadducts **10** and **11**



**10**



**11**

| compd | X | Y | $\delta_A$ | $\delta_B$ | $\delta_C$ | $\delta_D$ | $\delta_X$[b] | $J_{AB}$ | $J_{CD}$ | $J_{AC}$ | $J_{AD}$ | $J_{BC}$ | $J_{BD}$ | $J_{AX}$ | $J_{BX}$ | $J_{CX}$ | $J_{DX}$[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **10a** | H | CN | 1.93 | 2.61 | 2.97 | 3.23 | 3.57 | 13.2 | 10.7 | 9.1 | 10.4 | 1.5 | 7.5 | 5.2 | 1.6 | | |
| **10b** | H | COOMe | 1.91 | 2.53 | 2.88 | 2.96 | 3.50 | 13.2 | 10.5 | 8.7 | 10.9 | 1.4 | 6.9 | 6.0 | 1.2 | | |
| **10c** | H | COOtBu | 1.89 | 2.45 | 2.88 | 2.95 | 3.38 | 13.2 | 10.2 | 8.3 | 11.4 | 1.5 | 6.7 | 6.1 | 1.3 | | |
| **10d** | H | $NO_2$ | 2.13 | 2.89 | 2.98 | 3.07 | 5.34 | 14.4 | 10.6 | 9.0 | 10.6 | 1.5 | 7.0 | 5.1 | 1.4 | | |
| **10e** | $CH_3$ | CN | 2.26 | 2.36 | 2.82 | 2.87 | | 12.8 | 10.8 | 9.7 | 9.7 | 2.4 | 7.8 | | | | |
| **11a** | H | CN | 2.33 | 2.59 | 3.08 | 3.18 | 2.99 | 13.2 | 10.6 | | | | | 10.3 | 5.2 | 8.6 | 7.2 |
| **11b** | H | COOMe | 2.20 | 2.54 | 3.03 | 3.07 | 2.92 | 13.2 | 10.3 | | | | | 12.4 | 4.9 | 7.0 | 10.5 |
| **11c** | H | COOtBu | 2.17 | 2.48 | 3.00 | 3.00 | 2.83 | 13.0 | *a* | | | | | 12.7 | 5.0 | av | 9.0[a] |
| **11e** | $CH_3$ | CN | 2.06 | 2.74 | 2.84 | 3.19 | | 14.0 | 11.2 | | | | | | | | |
| **11f** | $CH_3$ | COOMe | 2.13 | 2.70 | 2.64 | 3.34 | | 14.0 | 11.0 | | | | | | | | |
| **11g** | $CH_3$ | COOtBu | 2.03 | 2.69 | 2.58 | 3.27 | | 13.9 | 11.0 | | | | | | | | |

[a] See discussion in text. [b] All $\delta$ values given in parts per million (ppm). [c] All $J$ values given in hertz.

Table III. Comparison between Experimental and Calculated $J_{vic}$ (Hz) Values for Cycloadducts **10a–c,e**

| | | | $J_{AX}$ | | $J_{BX}$ | | $J_{AC}$ | | $J_{AD}$ | | $J_{BC}$ | | $J_{BD}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | X | Y | exp | calcd | exp | calcd | exp | calcd | exp | calcd | exp | calcd | exp | calcd |
| **10a** | H | CN | 5.2 | 3.2 | 1.6 | 2.7 | 9.1 | 8.3 | 10.4 | 11.3 | 1.5 | 0.3 | 7.5 | 7.5 |
| **10b** | H | COOMe | 6.1 | 5.2 | 1.2 | 1.6 | 8.7 | 10.9 | 11.0 | 8.1 | 1.3 | 1.1 | 6.9 | 10.2 |
| **10c** | H | COOtBu | 6.1 | 7.2 | 1.3 | 1.0 | 8.3 | 11.6 | 11.4 | 5.9 | 1.5 | 1.7 | 6.7 | 11.0 |
| **10e** | $CH_3$ | CN | | | | | 9.7 | 7.1 | 9.7 | 12.4 | 2.4 | 0.6 | 7.8 | 6.0 |

low conversions to polymer, up to 3.6%, suggest that the stepwise reaction is still unimportant.

Even if the presence of two isomers, **10a–c** and **11a–c**, is easily seen from both $^1$H and $^{13}$C NMR, the assignment of the regioisomer proved to be rather difficult due to the very complex coupling pattern. The complete analysis was finally achieved by using resolution enhancement experiments on a 500-MHz spectrometer. A second-order $^1$H NMR spectrum was observed for **10f**; all of the NMR data are summarized in Table II.

The analysis of the $^1$H NMR spectra of the cycloadducts **11e–g** with an electron-withdrawing and a methyl substituent at $C_7$ is straightforward: each proton signal is a doublet and the $CH_2S$ system can be easily distinguished from the $CH_2$ system. The assignment of each proton is based on its chemical shift, taking into account the deshielding effect of the thioether and ester groups; the doublet farthest downfield is assigned to $H_D$ ($\alpha$ to the sulfur and cis to the ester) and the most upfield assigned to $H_A$ ($CH_2$ and trans to the ester). The spectra of cycloadducts **11a,b** are more complicated, but their analysis requires less assumption. $H_X$ is characterized by its doublet of doublet of doublet of doublet pattern; the $CH_2S$ protons can be distinguished from the $CH_2$ protons both by the geminal coupling constant ($J_{AB} > J_{CD}$) and the chemical shifts. The final assignment between $H_A$ and $H_B$, and $H_C$ and $H_D$ is based on the reasonable assumption of a larger chemical shift for the proton cis to the polar group (CN or COOR). The spectrum of **11c** is less easy to analyze because $H_C$ and $H_D$, the $CH_2S$ protons, have the same chemical shift ($\delta$ 3.00) and therefore no geminal coupling. It is known that protons with the same chemical shift will average out the coupling with a third proton, $H_X$ in this case, and only an apparent coupling constant will be observed, which is the average of the two expected values. Therefore, only a doublet ($J_{app}$ = 9 Hz) is observed for $CH_2S$ and $H_X$ is a doublet of doublet of triplet.

The value of each coupling constant for the protons of the cycloadducts **10a–e** could be determined, but the signal could not be immediately assigned to each proton. To solve this problem, theoretical vicinal coupling constants were calculated by applying modified Karplus relationships[25,26] on models of **10a**, **10b**, **10c**, and **10e**, with geometrical parameters previously optimized using the SYBYL Tripos Force Field molecular mechanics program. Comparisons between theoretical and experimental coupling constants were performed using different combinations. The best set is represented in Table III; it gives a mean difference between theoretical and experimental coupling constants of 1.8 Hz. The assignment is also compatible with the predictable change of the chemical shifts depending on the proximity of the ester group.

$^{13}$C NMR and IR spectra and elemental analyses were in agreement with the proposed structures. As has been noticed before,[18] the radical cations of the spirocycloadducts of TTCM lose dimethylketene. In the MS of the acrylonitrile adduct **10a**, M – $(CH_3)_2C{=}C{=}O$ ($m/z$ 153) is the base peak, and dimethylketene also occurs as radical cation. M – $(CH_3)_2C{=}C{=}O$ can aromatize by elimination of HCN; the radical cation of 2-isopropylthiophene ($m/z$ 126, 44) is a major fragment.

The use of acrylates or acrylonitriles bearing bulkier $\alpha$-groups than methyl, like ethyl or higher homologues, was precluded by the known very low polymerizability of these olefins above room temperature.[27] A further increase in the bulkiness of the olefin would not necessarily enhance the amount of polymer. The concerted pathway to the 7-substituted thiolane **11** is not burdened by steric interference and allows the system to avoid the formation of the intermediate.

It was impossible to use very electrophilic olefins like methylenemalononitrile, methylenemalonic esters, or $\alpha$-cyanoacrylic esters in these experiments; these olefins polymerize readily even in the presence of very weak nucleophiles.[28] Functionalities like the thioether or the azo group in the thiadiazoline **7**, the precursor of TTCM, or the ring sulfur of the thiolanes **10** and **11** are nucleophilic enough to induce polymerization. A blank experiment with methyl $\alpha$-chloroacrylate showed spontaneous polymerization at 45 °C. Methacrylates are known to polymerize through the

(25) PCMODEL; Serena Software; Box 3076, Bloomington, IN 47402-3076.

(26) Haasnoot, C. A. G.; DeLeeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.

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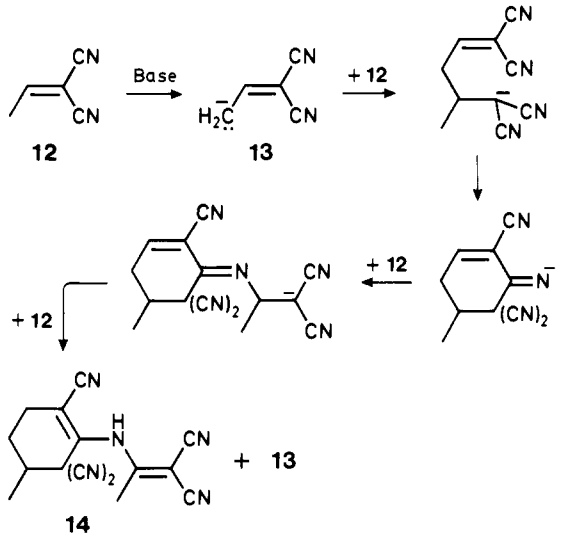
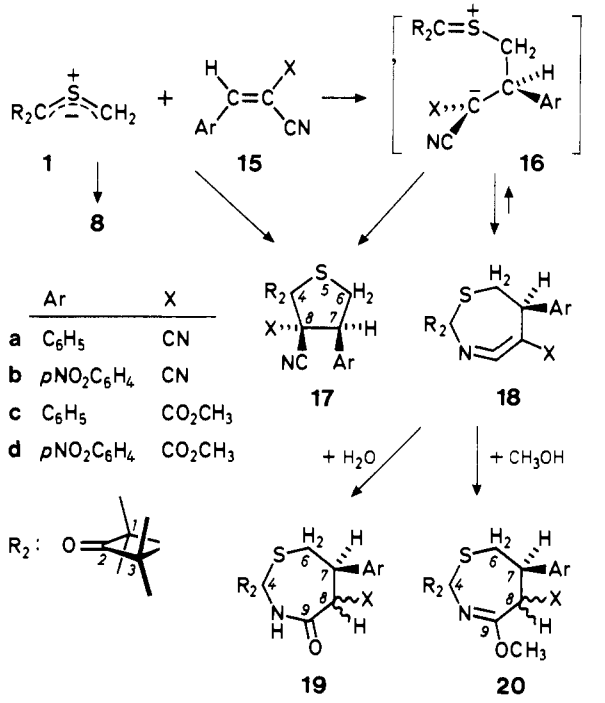
**Scheme IV**



**Scheme V**



initial formation of 1,4-tetramethylene diradical intermediates.[29] Therefore, the spontaneous polymerization of α-chloroacrylates can safely be ascribed to a 1,4-diradical which would be even more stabilized. α-Chloroacrylonitrile produced no polymer in the presence or absence of TTCM. At least three cycloadducts were formed, but not isolated.

Olefins without a free methylene end do not polymerize easily; at best they can oligomerize. When ethylidenemalonitrile was tried, some oligomers were produced. The cyclic trimer **14** was isolated and characterized, but a blank experiment proved that its origin was not connected to the presence of TTCM. Ethylidenemalononitrile is known to be sensitive to weak bases, but the reported structures of the oligomers are different from **14**.[30] Trimer **14** is most probably formed by adventitious base catalysis, as depicted in Scheme IV.

**Attempted Trapping of the Intermediate in the Reaction Between TTCM and Benzylidenemalononitrile and Related Compounds.** In the previous experiments, all olefins acted both as the dipolarophile leading to the intermediate and as the solvent responsible for the trapping of this intermediate. Is it possible to use a polymerizable olefin as the solvent during the cycloaddition of TTCM with an unpolymerizable dipolarophile that leads to an intermediate? To test this idea, the reactivity of benzylidenemalononitrile **15a** was investigated (Scheme V).

After **7** was heated with 1.1 equiv of **15a** in absolute THF for 3 h at 50 °C, $^1$H NMR analysis indicated the formation of 60% thiolane **17a** and 7% thiirane **8**, while after 8 h at 45 °C, 50% **17a** and 4% **8** were formed; the yield of **17a** reached 80% with acetonitrile as the solvent. The $^1$H NMR coupling pattern (ABC type) revealed the regiochemistry. As expected, no polymer had formed.

When the reaction was run in THF containing 1 vol % of *methanol* (8 h at 45 °C), the yields of **17a** and **8** decreased to 44% and 4%, respectively, and in addition, 21% of two methyl imidates **20a** containing 7-membered rings was formed. A tentative assignment as cis and trans with respect to stereocenters 7 and 8 can be based on the high-field shift which 7-phenyl exerts upon the cis-vic 8-H (in the trans form): δ 5.34 in **20aA** vs 4.98 in **20aB**. The $J_{7,8}$ values, 5.7 Hz for **A** and 11.1 Hz for **B**, would hint at the opposite assignment. The δ(OCH$_3$) values differ little (3.75, 3.81). **A** and **B** occurred in a 3:1 ratio.

The lactim methyl ethers **20a** originate from the interception of ketene imine **18a** by methanol (Scheme V). The analogy with the ketene imine **3c** from TTCM and tetracyanoethylene is obvious; **5c** is captured by methanol or water affording **6c** and the corresponding lactam.[9]

The interaction of TTCM with **15a** in THF containing 3 vol % of *water* (3 h at 50 °C) furnished 42% thiolane **17a** and 42% of a pair of 7-membered lactams **19a**, **A**:**B** = 78:22 ($^1$H NMR analysis). The diastereoisomers of **19a** were separated by fractional crystallization. The IR spectra show N–H bands, and the amide I frequency is at 1685 cm$^{-1}$; the amide II absorption is missing, as is customary for lactams of ring sizes 5–8.[31] The $^1$H NMR features are similar as stated above for **20a**: δ(8-H) 4.73 and $J_{7,8}$ = 6.5 Hz for **19aA**, δ 4.43 and 11.4 Hz for **19aB**. The equilibration of the diastereoisomers of **19a** is base-catalyzed. In CD$_3$CN a spontaneous isomerization was observed; **A** → **B** reached 35% in 2 days at room temperature.

The interception products **19a** and **20a** left no doubt that the cycloadditions proceeded, at least in part, through the zwitterionic intermediate **16a**. However, replacing THF by acrylonitrile as the solvent (8 h, 45 °C) did not induce the polymerization of acrylonitrile. The ratio of the acrylonitrile adducts **10a** and **11a** versus the benzylidenemalononitrile adduct **17a** was 75:25. A competition experiment determined the relative rate constants for the cycloadditions of TTCM: benzylidenemalononitrile reacts 33 times faster than acrylonitrile.

Malononitrile-type anions are known to induce polymerization of olefins activated by an α-acceptor group.[32] The absence of polyacrylonitrile probably means that the addition of acrylonitrile to the anionic portion of zwitterion **16a** is slow compared with the ring closures giving **17a** and **18a**. Acrylonitrile is more polar than THF, as Reichardt's $E_T$ values of 46.7 and 37.4, respectively, indicate.[33] Hence, a solvent effect cannot be invoked to explain the absence of polymerization.

Thus, two electron-attracting CN groups in 1,1-position of ethylene **15a** are sufficient to turn on the zwitterion mechanism; the "one-bond" electrophilicity[34] requires electron-attracting substituents at *one* of the ethylenic carbon atoms. One cyano group is inadequate; the reaction of TTCM with acrylonitrile and 3 vol % water did not give rise to an 8-membered lactam; only thiolane **10a** was obtained. The absence of polymerization (Table

(29) Lingnau, J.; Meyerhoff, G. *Macromolecules* **1984**, *17*, 941. *Makromol. Chem.* **1984**, *185*, 587.
(30) Weyr, M. R. S.; Hyne, J. B. *Can. J. Chem.* **1965**, *43*, 722.
(31) Huisgen, R.; Brade, H.; Walz, H.; Glogger, I. *Chem. Ber.* **1957**, *90*, 1437.
(32) Reetz, M. T.; Knauf, T.; Minet, U.; Bingel, C. *Angew. Chem.* **1988**, *100*, 1422; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1373.
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(34) Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937.

I) is a further argument. The 1,5- and 1,7-cyclizations of zwitterion **16** leading to thiolane **17** and ketene imine **18** are *intramolecular* alkylations of a cyano-substituted carbanion. *Intermolecular* analogues affording α-alkylnitriles or ketene imines are likewise known.[35] As Scheme V suggests, two pathways, a concerted and a two-step, may lead to thiolane **17**. The nonstereospecificity, mentioned in the Introduction, demands that at least part of **17** arises from an intermediate capable of rotation, like **16**.

Some other acceptor olefins related to **15a** were also included in this study: (4-nitrobenzylidene)malononitrile (**15b**), methyl α-cyanocinnamate (**15c**), and its 4-nitro derivative **15d**. All afforded crystalline thiolanes **17** in the reaction with TTCM in the absence of methanol or water. Inter- and intramolecular reactions of TTCM are competing; e.g., 66% thiolane **17c** and 15% thiirane **8** were obtained in THF, whereas 85% **17c** and 2% **8** resulted in acetonitrile. Due to the presence of two stereocenters, two diastereoisomers of **17c** and **17d** are conceivable, but just one was isolated. Since the 80-MHz $^1$H NMR spectra show additional signals and the balances are not quantitative, minor amounts of a second isomer cannot be excluded. The $^1$H NMR splitting pattern (dd for 7-H) clarifies the direction of addition. The occurrence of the 4-nitrostyrene radical cation ($m/z$ 149, 31) in the MS of **17b** and that of styrene (104, 100) in the MS of **17c** confirms the regiochemistry.

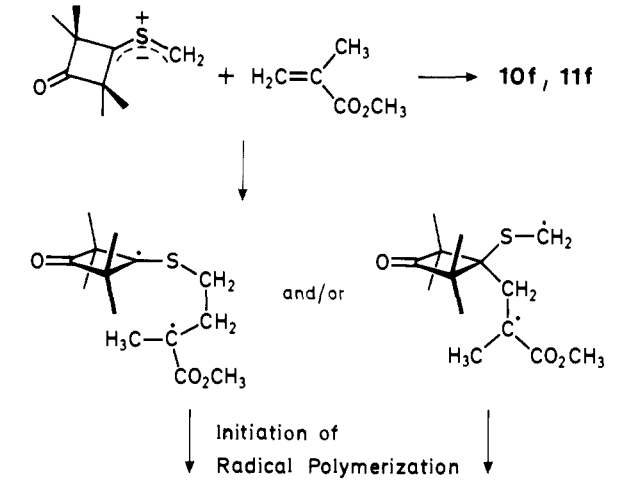
When TTCM was generated from **7** in THF and 3 vol % water, **15b–d** were converted to comparable amounts of thiolanes **17** and lactams **19** as described for **15a**. Thick-layer chromatography and fractional crystallization allowed the separation of the pairs of diastereoisomers of **19b–d**; all the lactams were obtained in pure form except **19bB**, of which only 5% was present. Like **19aA** and **B**, the lactams of the **A** series showed higher δ(8-H) than those of isomers **B**; $J_{7,8}$ values of 6.0–6.8 Hz for **A** and 10–11.4 Hz for **B** characterized stereochemical consistency.

**Analysis of the Polymers.** All polymers gave $^1$H NMR and IR spectra that are compatible with the proposed structures. SEC analysis of poly(methyl methacrylate) and poly(*tert*-butyl methacrylate) showed that both polymers have molecular weights larger than 1 500 000. The solubility of poly(methacrylonitrile) samples in different solvents was too low to allow detection of a polymer peak with our refractive index detector.

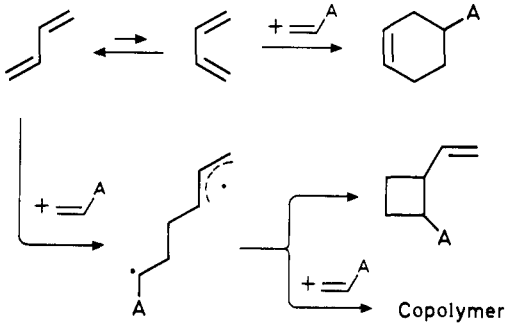
**Origin of the Polymerization.** As mentioned in the Introduction, a nonconcerted cycloaddition can be accompanied by a polymerization; a necessary condition for this to be true is evidently that at least one of the two partners is polymerizable. [2 + 2] cycloadditions, for which a concerted pathway is difficult to reach, have been studied in this respect.[5,6] Certain Diels–Alder reactions are also known to give substantial amounts of polymers when run in concentrated solutions and in the absence of polymerization inhibitors.[36–39] Even the very simple reaction between acrylonitrile and isoprene was initially run by Alder in the presence of hydroquinone.[36] Without this precaution, the yield of cycloadduct was found to drop dramatically; instead, a substantial quantity of polymer forms in a reproducible manner, and we have proposed a diradical intermediate as the initiator.[38] Some other examples of competition between cycloaddition and polymerization have been reviewed; they formed the basis of the "Bond-Forming Initiation" theory.[5,6]

In the same way, the known ability of TTCM to react in a zwitterionic fashion with very electrophilic olefins[9–11,14,15] originally led us to the conclusion that the polymerization had the same origin, i.e., the zwitterionic intermediate of type **3**. However, inhibition experiments on the polymerization of methyl methacrylate induced by TTCM demonstrated that the polymerization

Scheme VI




Scheme VII




was radical in nature. This result can be rationalized on the basis of the known very large difference in electrophilicity between ethylenes tetrasubstituted with electron-withdrawing groups like TCNE and a monosubstituted analogue like methacrylonitrile. With such different reactants, a change in the nature of the intermediate to diradical is analogous to the shift from zwitterionic to diradical intermediates observed in the [2 + 2] cycloadditions, which has been shown to be governed by the nature of the substituents on the olefins.[40] Therefore, the mechanism depicted for methyl methacrylate in Scheme VI is proposed for the observed polymerizations.

The low conversion for the polymerization can be explained by the small number of trapped diradicals. This means that the cycloadditions remain essentially concerted or that the ring closure of the diradical is rapid compared with the initiation of the polymerization. As other methods developed to investigate the nonconcerted character of cycloadditions, our method is not able to distinguish between these two alternatives. However, it seems reasonable to consider that the cycloaddition leading to the unexpected cycloadduct **11** is concerted; the putative diradical intermediate is not kinetically stabilized by the bulky tetramethyloxocyclobutyl radical.

The very high molecular weights of the polymers are remarkable and can also be ascribed to the small number of initiating diradicals. No termination by recombination will occur in these conditions, and the high concentration of monomer favors the propagation.

As described above, butadienes give substantial yields of polymers when mixed with simple olefins like acrylonitrile.[38] In contrast, our experiments demonstrate that a 1,3-dipole like TTCM only gives low conversions in polymers, even though it is known from other experiments to give stepwise cycloadditions. A possible explanation (Scheme VII) for this difference between the two [4 + 2] cycloadditions is that a butadiene needs to go through the planar s-cis conformation before undergoing cyclo-

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(38) Hall, H. K., Jr.; Padias, A. B.; Li, Y.; Clever, H. A.; Wang, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1279. Clever, H. A.; Wang, G.; Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.*, submitted for publication.
(39) Stepek, J. *Collect. Czech. Chem. Commun.* **1964**, *29*, 390.
(40) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117 and 199.

addition in a Diels–Alder manner with the dienophile; the s-trans conformer of the diene is unable to give the concerted cycloaddition but is still able to react with another olefin to give an intermediate. In contrast, 1,3-dipoles are three-atom systems that are linear or slightly bent.[7] As a consequence, the geometry that they need to adopt in the transition state of the concerted pathway is not very far away from their original geometry.

## Conclusion

It was shown that the thiocarbonyl ylide TTCM **1** is able to initiate the polymerization of olefins like methacrylates and methacrylonitrile. The polymerization competes with the normal cycloaddition, and we propose that it is initiated by a diradical intermediate. The present study constitutes a new experimental demonstration for the efficiency of trapping by polymerizable olefins. Using this new trapping technique, zwitterions or diradicals can be detected thanks to the amplification effect associated with the polymerization. Its experimental simplicity and the possibility to trap a very small quantity of intermediates with short half-lives make it a new general technique for studying the mechanism of cycloadditions. It is hoped that this and associated works[38] will stimulate the use of this trapping technique and favor the discovery of new nonconcerted cycloadditions.

## Experimental Section

**Instrumentation.** $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker Model WM-250 Multinuclear FT spectrometer at 250 MHz, on a Model AM 500 at 500 MHz, or on a Model WP 80 at 80 MHz in deuterated chloroform with tetramethylsilane as the internal standard (s, singlet; d, doublet; t, triplet; q, quadruplet). Infrared spectra were obtained with a Perkin-Elmer Model 983 spectrometer. Elemental analyses were performed by Helmut Schulz and Magdalena Schwarz, Munich, as well as by Desert Analytics, Tucson, AZ.

**Chemicals.** Nitroethylene and 2-nitropropene were synthesized respectively from 2-nitroethanol and 2-nitropropan-1-ol.[23,41] The other monomers are commercially available; they were purified by classical techniques (generally, they were washed with a basic aqueous solution to remove the inhibitor and then washed with water, dried, and distilled). Known procedures were used for the synthesis of (4-nitrobenzylidene)-malononitrile (**15b**),[42] methyl α-cyanocinnamate (**15c**),[43] and methyl α-cyano-4-nitrocinnamate (**15d**).[44] THF was distilled from sodium/benzophenone ketyl immediately prior to use.

**7,8-Diaza-1,1,3,3-tetramethyl-5-thiaspiro[3.4]oct-7-en-2-one (7)** was prepared by Diebert[17] as an "unstable intermediate" at −60 °C, reacted in situ in ethereal solution, and was not analyzed. We passed gaseous diazomethane into the solution of 468 mg (3.0 mmol) of 2,2,4,4-tetramethyl-3-thioxocyclobutanone[45] in 10 mL of ether at −78 °C until the red color of the thione was replaced by yellow. The excess of diazomethane was flushed out with $N_2$ and the solvent evaporated at 20 °C. The residue was crystallized from 10 mL of pentane at −78 °C; after 30 min, 520 mg (87%) of colorless **7** was obtained, mp 40–42 °C dec. Recrystallized, the thiadiazoline can be stored at −20 °C for several weeks: $^1H$ NMR ($CDCl_3$) δ 1.23 (s, 2 $CH_3$), 1.31 (s, 2 $CH_3$), 5.84 (s, 6-$H_2$). Anal. Calcd for $C_9H_{14}N_2OS$: C, 54.51; H, 7.12; N, 14.13; S, 16.17. Found: C, 54.39; H, 7.15; N, 14.19; S, 16.18.

**Reactions of 7 with the Polymerizable Olefins. General Procedure.** The olefin (2 mL) and $3 \times 10^{-4}$ mol of **7** were mixed in a polymerization tube. The solution was degassed by a freeze–purge–thaw procedure (3 times) using argon as an inert gas. After 8 h at 44 °C, the excess of the olefin was removed by evaporation at low pressure. The residue was purified by specific procedures described below. If a polymer had formed during the reaction, the residue was dissolved in 2 mL of acetone and the polymer was reprecipitated in 50 mL of methanol. The filtrate was evaporated, and the final residue consisting of low-molecular-weight products was then purified.

The yield of the low-molecular-weight products was determined in a separate experiment by quantitative $^1H$ NMR using 1,1,2,2-tetrachloroethane as the standard. The yields of the polymers are calculated from the initial amount of the olefin.

**Reaction with Acrylonitrile.** No polymer. The residue was chromatographed on silica gel using 1,2-dichloroethane as the eluent. A mixture of **10a** and **11a** (ratio = 4.0) was isolated. Analytical yield = 79%. Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67; N, 6.27. Found: C, 64.51; H, 7.53; N, 6.19. When working with larger quantities (2.0 mmol of **7** in 4 mL of acrylonitrile) at 50 °C over 5 h, $^1H$ NMR analyses with a weighed standard ($ClHC{=}CCl_2$) gave 78% **10a** (δ 1.61, s) and 16% **11a** (δ 1.20, s). After repeated evaporation with ethanol, the cycloadduct **10a** crystallized from 5 mL of ethanol at −70 °C (40%), mp 57–58 °C ($CH_2Cl_2$/hexane), colorless needles: IR (KBr) 2237 (C≡N), 1773 (C=O), 1461, 1380, 1163, 1021 $cm^{-1}$; MS (70 eV, 35 °C) *m/z* 223 (M, <1), 153 (M − $(CH_3)_2C{=}C{=}O$, 100), 138 (153 − $CH_3$, 23), 126 (153 − HCN, 2-isopropylthiophene, 44), 85 (22), 70 ($(CH_3)_2C{=}C{=}O$, 15). Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67; N, 6.27; S, 14.36. Found: C, 64.77; H, 7.63; N, 6.10; S, 14.34.

1,1,3,3-Tetramethyl-2-oxo-5-thiaspiro[3.4]octane-8-carbonitrile (**10a**): $^1H$ NMR δ 3.57 (dd, 1 H, 5.2 Hz, 1.6 Hz), 3.23 (td, 1 H, 10.6 Hz, 7.5 Hz), 2.97 (ddd, 1 H, 10.7 Hz, 9.1 Hz, 1.6 Hz), 2.61 (ddt, 1 H, 13.2 Hz, 7.5 Hz, 1.5 Hz), 1.93 (dddd, 1 H, 13.2 Hz, 10.4 Hz, 9.1 Hz, 5.2 Hz), 1.61 (s, 3 H), 1.31 (s, 3 H), 1.30 (s, 6 H); $^{13}C$ NMR δ 218.4 (C=O), 119.8 (CN), 67.9, 65.2, 61.2, 38.7, 33.7, 28.6, 23.5, 22.8, 22.2, 20.2.

1,1,3,3-Tetramethyl-2-oxo-5-thiaspiro[3.4]octane-7-carbonitrile (**11a**): $^1H$ NMR δ 3.18 (dd, 1 H, 10.6 Hz, 7.3 Hz, 0.5 Hz), 3.08 (dd, 1 H, 10.6 Hz, 8.8 Hz), 2.99 (dddd, 1 H, 10.3 Hz, 8.6 Hz, 7.2 Hz, 5.2 Hz), 2.59 (ddd, 1 H, 13.2 Hz, 5.1 Hz, 0.4 Hz), 2.33 (dd, 1 H, 13.3 Hz, 10.3 Hz), 1.33 (s, 3 H), 1.32 (s, 3 H), 1.25 (s, 3 H), 1.20 (s, 3 H); $^{13}C$ NMR δ 219.8 (C=O), 119.7 (CN), 65.0, 63.7, 62.9, 40.2, 34.3, 32.3, 24.8, 24.1, 20.7, 19.4.

**Reaction with Methyl Acrylate.** No polymer. The residue was chromatographed on silica gel, using a mixture of petroleum ether/ethyl acetate, 90:10 v/v, as the eluent. A mixture of **10b** and **11b** was isolated. Analytical yield = 96%. Anal. Calcd for $C_{12}H_{20}O_3S$: C, 60.90; H, 7.86. Found: C, 61.20; H, 7.80. When working with larger quantities (2.0 mmol of **7** in 4 mL of methyl acrylate) at 50 °C over 5 h, the 400-MHz $^1H$ NMR spectrum ($CDCl_3$) indicated **10b** and **11b** in a 65:35 ratio; the $CH_3$ singlets at δ 1.35 for **10b** and at 1.18 for **11b** were integrated, and thiirane **8** was not formed. The oily product was twice dissolved in methanol and evaporated. On cooling the solution in 2 mL of methanol to −78 °C, colorless needles (97 mg, 19%) of **11b** were obtained, mp 82–83 °C after recrystallization from methanol at −20 °C. The residue of the mother liquor was dissolved in 3 mL of pentane; after 24 h at −78 °C, colorless prisms (170 mg, 33%) of **10b**, mp 40–45 °C, were filtered. Recrystallization from pentane furnished pure **10b**, mp 49–50 °C.

Methyl 1,1,3,3-tetramethyl-2-oxo-5-thiaspiro[3.4]octane-8-carboxylate (**10b**): IR (KBr) 1786 (C=O, ketone), 1738 (C=O, ester), 1462, 1442, 1364, 1196, 1165 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) δ 1.28, 1.29, 1.33, 1.35 (4s, 4 $CH_3$), 1.92 (dddd, 13.2 Hz, 11.0 Hz, 8.7 Hz, 6.1 Hz, 7-$H_A$), 2.52 (ddt, 13.2 Hz, 6.9 Hz, 1.2 Hz, 7-$H_B$), 2.88 (ddd, 10.3 Hz, 8.7 Hz, 1.3 Hz, 6-$H_C$), 2.96 (dt, 10.7 Hz, 6.9 Hz, 6-$H_D$), 3.50 (broad td, 6.1 Hz, 1.2 Hz, 8-$H_X$), 3.72 (s, $OCH_3$); $^{13}C$ NMR ($CDCl_3$) δ 20.7, 22.8, 22.9, 23.6 (4 $CH_3$), 29.6, 34.2 (C-6, C-7), 50.8 (C-8), 51.9 ($OCH_3$), 61.3, 65.4, 67.9 (C-1, C-3, C-4), 172.8 (CO, ester), 220.9 (CO, ketone). Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.90; H, 7.86; S, 12.51. Found: C, 61.09; H, 7.86; S, 12.57.

Methyl 1,1,3,3-tetramethyl-2-oxo-5-thiaspiro[3.4]octane-7-carboxylate (**11b**): IR (KBr) 1767 (C=O, ketone), 1724 (C=O, ester), 1239, 1204, 1179, 1030 (CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) δ 1.18, 1.21, 1.30, 1.32 (4s, 4 $CH_3$), 2.20 (t, 12.8 Hz, 8-$H_A$), 2.54 (dd, 13.1 Hz, 5.0 Hz, 8-$H_B$), 2.88–2.97 (m, 7-$H_X$), 3.01–3.10 (m, AB part of ABC, 6-$H_2$); $^{13}C$ NMR ($CDCl_3$) δ 19.0, 20.5, 24.3, 25.1 (4 $CH_3$), 33.0, 39.8 (C-6, C-8), 47.9 (C-7), 52.2 ($OCH_3$), 62.1, 63.9, 65.0 (C-1, C-3, C-4), 173.1 (CO, ester), 221.2 (CO, ketone). Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.90; H, 7.86; S, 12.51. Found: C, 60.77; H, 7.88; S, 12.58.

**Reaction with *tert*-Butyl Acrylate.** The solid residue was recrystallized from pentane at −50 °C. A mixture of the two regioisomers, **10c** and **11c** (ratio = 0.3), was isolated as a white powder. Isolated yield = 74%. Analytical yield = 97%. Anal. Calcd for $C_{16}H_{26}O_3S$: C, 64.39; H, 8.78. Found: C, 64.61; H, 8.86. IR ($CHCl_3$) 1769 (C=O), 1719 (ester) $cm^{-1}$.

*tert*-Butyl 1,1,3,3-tetramethyl-2-oxo-5-thiaspiro[3.4]octane-8-carboxylate (**10c**): $^1H$ NMR 3.38 (dd, 1 H, 6.1 Hz, 1.3 Hz), 2.95 (ddd, 1 H, 11.3 Hz, 10.2 Hz, 6.7 Hz), 2.88 (ddd, 1 H, 10.1 Hz, 8.5 Hz, 1.5 Hz), 2.45 (ddt, 1 H, 13.1 Hz, 6.6 Hz, 1.4 Hz), 1.89 (dddd, 13.3 Hz, 11.4 Hz, 8.2 Hz, 6.2 Hz), 1.59 (s, 3 H), 1.48 (s, 9 H), 1.38 (s, 3 H), 1.31 (s, 3 H), 1.27 (s, 3 H); $^{13}C$ NMR 221.1 (C=O), 171.5 (O—C=O), 80.7, 67.7, 65.1, 61.3, 51.8, 34.6, 29.6, 27.9, 23.7, 22.8, 22.8, 20.4.

*tert*-Butyl 1,1,3,3-tetramethyl-2-oxo-5-thiaspiro[3.4]octane-7-carboxylate (**11c**): $^1H$ NMR δ 3.00 (d, 2 H, 9.0 Hz(av)), 2.83 (dtd, 1 H, 12.6 Hz, 9.0 Hz(av), 5.0 Hz), 2.48 (dd, 1 H, 13.1 Hz, 5.0 Hz), 2.17 (t, 1 H, 12.8 Hz), 1.47 (s, 9 H), 1.32 (s, 3 H), 1.30 (s, 3 H), 1.19 (s, 3 H); $^{13}C$ NMR δ 221.1 (C=O), 171.8 (O—C=O), 81.2, 64.9, 63.8, 61.9,

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49.0, 39.4, 33.0, 27.9, 24.9, 24.1, 20.4, 18.9.

**Reaction with Nitroethylene.** Poly(nitroethylene) was isolated in yields varying between 1.4 and 2.8%. The residue was purified by chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (90:10 v/v). The product decomposed slowly on silica gel; however, it was stable for at least 1 month at room temperature. 8-Nitro-1,1,3,3-tetramethyl-5-thiaspiro[3.4]octan-2-one (**10d**): $^1$H NMR $\delta$ 5.34 (dd, 1 H, 5.0 Hz, 1.4 Hz), 3.07 (td, 1 H, 10.6 Hz, 7.0 Hz), 2.98 (ddd, 1 H, 10.7 Hz, 9.0 Hz, 1.6 Hz), 2.89 (ddt, 1 H, 14.5 Hz, 7.0 Hz, 1.4 Hz), 2.13 (dddd, 14.4 Hz, 10.5 Hz, 9.1 Hz, 5.1 Hz), 1.41 (s, 3 H), 1.36 (s, 3 H), 1.31 (s, 3 H), 1.30 (s, 3 H); $^{13}$C NMR $\delta$ 218.4 (C=O), 90.9 ($CHNO_2$), 66.6, 62.2, 36.5, 28.6, 22.8, 22.5, 22.4, 20.8 (comment: one of the quaternary carbons could not be detected, even after a long accumulation time); IR ($CHCl_3$) 1785 (C=O), 1558 ($NO_2$) cm$^{-1}$.

**Reaction with Methacrylonitrile.** 0.2% Poly(methacrylonitrile). The residue was chromatographed on silica gel, using a mixture of petroleum ether/1,2-dichloroethane, 50:50 v/v, as the eluent. A mixture of two regioisomers, **10e** and **11e** (ratio = 1.0), was isolated. Pure **11e** can be obtained by repetitive recrystallization in hexane at −50 °C. Analytical yield = 36%; 57% thiirane **8** was also formed during the reaction. Anal. Calcd for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; N, 5.90. Found: C, 65.84; H, 8.03; N, 5.72. IR ($CHCl_3$) 2239 (CN), 1774 (C=O) cm$^{-1}$.

1,1,3,3,8-Pentamethyl-2-oxo-5-thiaspiro[3.4]octane-8-carbonitrile (**10e**): $^1$H NMR $\delta$ 2.87 (ddd, 1 H, 10.8 Hz, 9.7 Hz, 7.9 Hz), 2.82 (td, 1 H, 10.3 Hz, 2.4 Hz), 2.36 (ddd, 1 H, 12.8 Hz, 7.8 Hz, 2.4 Hz), 2.26 (dt, 1 H, 12.8 Hz, 9.7 Hz), 1.78 (s, 3 H), 1.75 (s, 3 H), 1.74 (s, 3 H), 1.43 (s, 3 H), 1.22 (s, 3 H).

1,1,3,3,7-Pentamethyl-2-oxo-5-thiaspiro[3.4]octane-7-carbonitrile (**11e**): $^1$H NMR $\delta$ 3.19 (dd, 1 H, 11.2 Hz, 0.8 Hz), 2.84 (d, 1 H, 11.1 Hz), 2.74 (dd, 1 H, 14.0 Hz, 0.8 Hz), 2.06 (d, 1 H, 13.9 Hz), 1.61 (s, 3 H), 1.40 (s, 3 H), 1.36 (s, 3 H), 1.26 (s, 3 H), 1.22 (s, 3 H); $^{13}$C NMR $\delta$ 220.8 (C=O), 123.6 (CN), 65.8, 64.6, 63.1, 47.0, 43.5, 43.3, 24.2, 23.8, 23.3, 21.9, 21.8.

**Reaction with Methyl Methacrylate.** 2.6% Poly(methyl methacrylate). The residue was chromatographed on silica gel with a Chromatotron, using a mixture of petroleum ether/ethyl acetate, 97:3 v/v, as the eluent. A mixture of two regioisomers, **10f** and **11f** (ratio = 0.4), was isolated. Analytical yield = 40%; 35% thiirane **8** was also formed during the reaction. Anal. Calcd for $C_{14}H_{22}O_3S$: C, 62.18; H, 8.20. Found: C, 62.04; H, 7.95. IR ($CHCl_3$) 1772 (C=O), 1725 (O—C=O) cm$^{-1}$.

Methyl 1,1,3,3,8-pentamethyl-2-oxo-5-thiaspiro[3.4]octane-8-carboxylate (**10f**): $^1$H NMR (500 MHz) $\delta$ 1.29 (s, 3 H), 1.43 (s, 3 H), 1.56 (s, 3 H), 1.59 (s, 3 H), 1.62 (s, 3 H), 1.92 (m, 1 H), 2.65 (m, 2 H), 2.80 (m, 1 H), 3.72 (s, 3 H); $^{13}$C NMR $\delta$ 220.4 (C=O), 175.2 (O—C=O), 69.4, 66.4, 59.5, 52.0, 41.6, 39.8, 25.2, 25.0, 24.4, 22.4, 21.8 (one of the quaternary carbons could not be observed, even after a long accumulation time).

Methyl 1,1,3,3,7-pentamethyl-2-oxo-5-thiaspiro[3.4]octane-7-carboxylate (**11f**): $^1$H NMR (500 MHz) $\delta$ 1.21 (s, 3 H), 1.25 (s, 3 H), 1.26 (s, 3 H), 1.27 (s, 3 H), 1.41 (s, 3 H), 2.13 (d, 1 H, 14 Hz), 2.64 (d, 1 H, 11 Hz), 2.70 (d, 1 H, 14 Hz), 3.34 (d, 1 H, 11 Hz), 3.73 (s, 3 H); $^{13}$C NMR $\delta$ 221.9 (C=O), 176.1 (O—C=O), 65.9, 63.8, 63.5, 54.4, 52.3, 44.6, 41.7, 23.9, 23.2, 23.7, 22.6, 21.9.

**Reaction with *tert*-Butyl Methacrylate.** 3.6% Poly(*tert*-butyl methacrylate). The residue was chromatographed on silica gel with a Chromatotron, using a mixture of petroleum ether/ethyl acetate; 98:2 v/v, as the eluent. **11g** was the only isomer. Analytical yield = 23%; 12% thiirane **8** was also formed during the reaction.

*tert*-Butyl 1,1,3,3,7-pentamethyl-2-oxo-5-thiaspiro[3.4]octane-7-carboxylate (**11g**): $^1$H NMR $\delta$ 1.22 (s, 3 H), 1.26 (s, 3 H), 1.27 (s, 3 H), 1.29 (s, 3 H), 1.37 (s, 3 H), 1.47 (s, 9 H), 2.03 (d, 1 H, 13.9 Hz), 2.58 (d, 1 H, 11.0 Hz), 2.69 (d, 1 H, 13.9 Hz), 3.27 (d, 1 H, 11.0 Hz); $^{13}$C NMR $\delta$ 222.2 (C=O), 174.9 (O—C=O), 81.0, 66.0, 63.7, 63.5, 55.1, 44.0, 41.8, 28.0, 24.1, 23.0, 22.7, 22.2; IR ($CHCl_3$) 1771 (C=O), 1713 (O—C=O) cm$^{-1}$. Anal. Calcd for $C_{17}H_{28}O_3S$: C, 65.34; H, 9.03. Found: C, 65.06; H, 8.87.

**Reactions with Nonpolymerizable Olefins. Reactions with Benzylidenemalononitrile (15a).** a. Precursor **7** (297 mg, 1.5 mmol) and 255 mg (1.65 mmol) of **15a** in 4 mL of absolute THF were heated in a 50 °C bath; after 3 h, $N_2$ evolution was finished. The solvent was removed under reduced pressure, and the residue was analyzed by $^1$H NMR in $CDCl_3$ with a weighed standard (*sym*-tetrachloroethane): 60% **17a** ($\delta$ 1.81, 1.85, 2 $CH_3$) and 7% thiirane **8** ($\delta$ 2.65, $CH_2$). A second experiment carried out in absolute acetonitrile furnished 80% **17a** and 2% **8**. Working with 0.25 mmol of **7** and 0.30 mmol of **15a** in 2 mL of absolute THF (45 °C, 8 h) afforded 50% **17a** and 4% **8**. The colorless 1,1,3,3-tetramethyl-2-oxo-7-phenyl-5-thiaspiro[3.4]octane-8,8-dicarbonitrile (**17a**) crystallized from methanol: mp 152–153 °C; IR (KBr) 2240 (vw, CN), 1781 (C=O), 704, 745 cm$^{-1}$ ($C_6H_5$ wagging); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.40, 1.57, 1.81, 1.85 (4s, 4 $CH_3$), 3.28 (dd, 11.2 Hz, 8.8 Hz, 6-$H_A$), 3.49 (broad t, $J \approx$ 10.8 Hz, 6-$H_B$), 3.69 (dd, $J$ = 10.2 nd 8.8 Hz, 7-H), 7.45–7.6 (m, $C_6H_5$); $^{13}$C NMR 21.1, 21.1, 23.2, 26.4 (4 $CH_3$), 31.2 (C-6), 50.4, 56.8 (C-7, C-8), 62.9, 68.1, 69.7 (C-1, C-3, C-4), 113.4, 114.7 (2 CN), 128.7, 129.3, 130.0, 132.4 ($C_6H_5$), 216 (C=O). Anal. Calcd for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.64; S, 9.88. Found: C, 70.38; H, 6.18; N, 8.78; S, 9.88.

b. **7** (50.4 mg, 0.25 mmol) and **15a** (47.6 mg, 0.30 mmol) in 2 mL of a 1 vol % solution of MeOH in THF were heated at 45 °C over 8 h. The residue was chromatographed on silica gel using a mixture of petroleum ether/$CH_2Cl_2$, 50:50 v/v, as the eluent. Products **17a** (analytical data described above), **20aA**, and **20aB** were isolated; the latter two were characterized as a mixture. Analytical yields: 44% **17a**, 16% **20aA**, 5% **20aB**, and 4% thiirane **8**.

10-Aza-9-methoxy-2-oxo-7-phenyl-1,1,3,3-tetramethyl-5-thia-9,10-dehydrospiro[3.6]decane-8-carbonitrile (**20a**): Anal. Calcd for $C_{20}H_{24}N_2O_2S$: C, 67.38; H, 6.79; N, 7.86. Found: C, 67.28; H, 6.70; N, 7.75. IR ($CHCl_3$) 2249 (C≡N), 1775 (C=O), 1689 (C=N).

10-Aza-9-methoxy-2-oxo-7-phenyl-1,1,3,3-tetramethyl-5-thia-9,10-dehydrospiro[3.6]decane-8-carbonitrile (**20aA**): $^1$H NMR $\delta$ 1.14 (s, 3 H), 1.41 (s, 3 H), 1.43 (s, 3 H), 1.45 (s, 3 H), 2.88 (dd, 1 H, 15.0 Hz, 11.6 Hz), 3.11 (dd, 1 H, 15.0 Hz, 6.9 Hz), 3.41 (ddd, 1 H, 11.6 Hz, 6.9 Hz, 5.7 Hz), 3.75 (s, 3 H, MeO), 5.34 (d, 1 H, 5.7 Hz), 7.1–7.4 (m, 5 H); isomer **20aB** $^1$H NMR $\delta$ 1.14 (s, 3 H), 1.33 (s, 3 H), 1.41 (s, 3 H), 1.47 (s, 3 H), 2.90 (dd, 1 H, 15.2 Hz, 2.0 Hz), 3.04 (dd, 1 H, 15.3 Hz, 6.8 Hz), 3.42 (ddd, 1 H, 11.1 Hz, 6.8 Hz, 2.0 Hz), 3.81 (s, 3 H, MeO), 4.98 (d, 1 H, 11.1 Hz), 7.1–7.4 (m, 5 H).

c. Precursor **7** (1.5 mmol) and 1.65 mmol of **15a** in 5 mL of THF and 0.15 mL of water were magnetically stirred for 3 h in a 50 °C bath. After evaporation of the solvent, the $^1$H NMR analysis ($CH_3CN$, ClH-C=$CCl_2$ as standard) indicated 42% **17a** and 42% of the lactams **19aA** ($\delta$ 4.43) and **19aB** ($\delta$ 4.73) in a 78:22 ratio. After evaporation, trituration with acetone left 20% **19aA**. The residue of the mother liquor was subjected to preparative thick-layer chromatography (henceforth PTLC) on silica gel with $CH_2Cl_2$/acetone 95:5; 30% **17a** came first, followed by the lactams. Fractional crystallization (ethanol) afforded 12% **19aA** and an additional 9% **19aB**.

10-Aza-1,1,3,3-tetramethyl-2,9-dioxo-7-phenyl-5-thiaspiro[3.6]decane-8-carbonitrile (**19aA**): mp 190–191 °C (ethyl acetate); IR (KBr) 3397, 3279 (NH), 2255 (w, CN), 1784 (C=O), 1685 (amide I), 1499 ($C_6H_5$ ring vibr), 1454, 1392, 1030, 736, 699 cm$^{-1}$ ($C_6H_5$ wagg); $^1$H NMR ($CD_3CN$) $\delta$ 1.32 (s, 2 $CH_3$), 1.47, 1.52 (2s, 2 $CH_3$), 2.87–3.62 (m, 6-$H_2$, 7-H), 4.73 (d, $J$ = 6.5 Hz, 8-H), 6.45 (br, NH), 7.25–7.5 ($C_6H_5$). Anal. Calcd for $C_{19}H_{22}N_2O_2S$: C, 66.64; H, 6.48; N, 8.18; S, 9.36. Found: C, 66.58; H, 6.60; N, 8.35; S, 9.37. Isomer **19aB**: mp 164–165 °C (ethanol); IR (KBr) 3403 (br, NH), 2256 (w, CN), 1786 (C=O), 1685 (amide I), 1497 ($C_6H_5$ vibr), 1390, 1028, 700, 785 cm$^{-1}$ ($C_6H_5$ wagg); $^1$H NMR ($CD_3CN$) $\delta$ 1.32 (s, 3 $CH_3$), 1.52 (s, $CH_3$), 2.75–3.75 (m, 6-$H_2$, 7-H), 4.43 (d, $J$ = 11.4 Hz, 8-H), 6.37 (br, NH), 7.25–7.5 ($C_6H_5$). Anal. Found: C, 66.35; H, 6.48; N, 8.25; S, 9.42.

**Reactions with (4-Nitrobenzylidene)malononitrile (15b).** a. The reaction in absolute THF was carried out as above. The $^1$H NMR analysis in $CDCl_3$ and acetone-$d_6$ (1:1) with *sym*-tetrachloroethane as a standard showed 66% **17b** ($\delta$ 3.1–3.9) and 8% thiirane **8**. Yellow crystals obtained from methanol required PTLC ($SiO_2$, $CH_2Cl_2$) for purification. 1,1,3,3-Tetramethyl-2-oxo-7-(*p*-nitrophenyl)-5-thiaspiro[3.4]octane-8,8-dicarbonitrile (**17b**) crystallized from methanol/$CH_2Cl_2$ (50:50 v/v) as colorless needles: mp 198–199 °C; IR (KBr) 2243 (vw, CN) 1786 (C=O), 1609, 1497 (arom ring vibr), 1524, 1352 ($NO_2$), 858 cm$^{-1}$ ($C_6H_4$ wagg); $^1$H NMR ($CDCl_3$) $\delta$ 1.40, 1.57, 1.80, 1.82 (4s, 4 $CH_3$), 3.1–3.58 (AB part of ABC, 6-$H_2$), 3.78 (dd, 8.8 Hz and 9.2 Hz, 7-H), 7.65, 8.25 (AA'BB', $C_6H_4$); MS (20 eV, 140 °C) $m/z$ 369 (M, <1), 299 (M − $(CH_3)_2C$=C=O, 33), 149 (*p*-nitrostyrene, 31), 70 (dimethylketene, 100). Anal. Calcd for $C_{19}H_{19}N_3O_3S$: C, 61.77; H, 5.18; N, 11.38; S, 8.68. Found: C, 61.74; H, 5.08; N, 11.29; S, 8.70.

b. Reaction in THF and 3 vol % water as above. $^1$H NMR analysis ($CD_3CN$, *sym*-$C_2H_2Cl_4$) showed 43% **17b**, 44% **19bA** ($\delta$ 4.75), and ~5% **19bB** (4.64). Trituration with $CH_2Cl_2$ gave colorless crystals of 10-aza-1,1,3,3-tetramethyl-2,9-dioxo-7-(*p*-nitrophenyl)-5-thiaspiro[3.6]decane-8-carbonitrile (**19bA**): mp 210–212 °C (acetonitrile); IR (KBr) 3405 (br, NH), 2253 (w, CN), 1786 (C=O), 1686 (amide I), 1607, 1497 (arom ring vibr), 1523, 1349 ($NO_2$), 857 cm$^{-1}$ ($C_6H_4$ wagg); $^1$H NMR ($CD_3CN$) $\delta$ 1.30, 1.35, 1.38, 1.46 (4s, 4 $CH_3$), 3.0–3.9 (m, 6-$H_2$, 7-H), 4.75 (d, 6.8 Hz, 8-H), 7.52, 8.15 (AA'BB', $C_6H_4$). Anal. Calcd for $C_{19}H_{21}N_3O_4S$: C, 58.90; H, 5.46; N, 10.85; S, 8.28. Found: C, 59.06; H, 5.47; N, 10.61; S, 8.25. In the isomer **19bB**, $\delta$(8-H) is at $\delta$ 4.64 with $J_{7,8}$ = 10 Hz.

**Reactions with Methyl α-Cyanocinnamate (15c).** a. After the reaction of 1.5 mmol of **7** in absolute THF (3 h, 50 °C), $^1$H NMR comparison with weighed *sym*-$C_2H_2Cl_4$ in $CDCl_3$ resulted in 73% **17c** ($\delta$ 3.63, $OCH_3$) and 15% **8** (2.57, $CH_2$); an experiment in acetonitrile furnished 85% **17c**

and 2% **8**. Methyl 8-cyano-1,1,3,3-tetramethyl-2-oxo-7-phenyl-5-thiaspiro[3.4]octane-8-carboxylate (**17c**) (315 mg, 59%) crystallized from methanol: mp 132–133 °C; IR (KBr) 2245 (w, CN), 1783 (C=O, ketone), 1737 (C=O, ester), 1496 (arom ring vibr), 1263, 1237 (CO), 741, 704 $cm^{-1}$ ($C_6H_5$ wagg); $^1H$ NMR ($CDCl_3$) $\delta$ 1.42, 1.47, 1.55, 1.70 (4s, 4 $CH_3$), 3.63 (s, $OCH_3$), 3.0–3.5 (AB part of ABX, 6-$H_2$), 4.09 (t, 9.2 Hz, 7-H), 7.1–7.6 (m, $C_6H_5$); MS (70 eV, 90 °C) *m/z* 326 (M – $OCH_3$, <1), 313 (7), 287 (M – $(CH_3)_2C{=}C{=}O$, 69), 224 (33), 183 (287 – styrene, 37), 151 ($(CH_3)_2C{=}C{=}C(CN)CO_2CH_3$, 33), 136 (151 – $CH_3$, 23), 104 (styrene, 100), 91 (46), 70 (dimethylketene, 21). Anal. Calcd for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92; S, 8.97. Found: C, 67.46; H, 6.35; N, 4.11; S, 8.94.

b. The product of the reaction in THF and 3% water could not be analyzed by $^1H$ NMR due to signal overlap. PTLC on $SiO_2$ with $CH_2Cl_2$ provided 53% thiolane **17c** and 30% of the diastereoisomer **19c** (**A**:**B** = 65:35); PTLC three times with $CH_2Cl_2$/acetone (95:5) resulted in their separation.

Methyl 10-aza-1,1,3,3-tetramethyl-2,9-dioxo-7-phenyl-5-thiaspiro-[3.6]decane-8-carboxylate (**19cA**): mp 171–173 °C (methanol); IR (KBr) 3240 (br, NH), 1786 (C=O, ketone), 1764 (C=O, ester), 1675 (amide I), 1498 (arom ring vibr), 1295, 1190, 1175, 1025 (CO, CN), 700, 766 $cm^{-1}$ ($C_6H_5$, wagg); $^1H$ NMR ($CDCl_3$) $\delta$ 1.38 (s, 2 $CH_3$), 1.42, 1.50 (2s, 2 $CH_3$), 2.75–3.50 (m, 6-$H_2$, 7-H), 3.58 (s, $OCH_3$), 4.31 (d, $J$ = 6.0 Hz, 8-H), 6.35 (NH), 7.1–7.4 ($C_6H_5$). Anal. Calcd for $C_{20}H_{25}NO_4S$: C, 63.97; H, 6.71; N, 3.73; S, 8.54. Found: C, 63.96; H, 6.71; N, 3.43; S, 8.57.

Isomer **19cB**: mp 187–188 °C (ether); IR (KBr) 3294 (br, NH), 1786 (C=O, ketone), 1758 (C=O, ester), 1669 (amide I), 1494 (arom ring vibr), 1388, 1287, 1121, 1153, 1031 (CO, CN), 699, 762 $cm^{-1}$ ($C_6H_5$ wagg); $^1H$ NMR ($CDCl_3$) $\delta$ 1.34, 1.36, 1.50, 1.60 (4s, 4 $CH_3$), 2.6–3.8 (m, 6-$H_2$, 7-H), 3.58 (s, $OCH_3$), 4.14 (d, $J$ = 10.5 Hz, 8-H), 6.25 (NH), 7.6–8.5 ($C_6H_5$). Anal. Found: C, 63.74; H, 6.70; N, 3.53; S, 8.53.

**Reactions with Methyl α-Cyano-4-nitrocinnamate (15d).** a. According to $^1H$ NMR analysis ($ClHC{=}CCl_2$, standard, $CDCl_3$), the product which resulted in absolute THF contained 70% **17d** ($\delta$ 3.65) and 3% **8**. Whether additional signals of the 80-MHz spectrum can be attributed to a stereoisomer is open. After removal of the solvent, treatment with a small volume of methanol left 65% colorless crystals undissolved. Methyl 8-cyano-1,1,3,3-tetramethyl-2-oxo-7-(*p*-nitrophenyl)-5-thiaspiro[3.4]octane-8-carboxylate (**17d**): mp 197–199 °C (ethyl acetate); IR (KBr) 2240 (vw, CN), 1784 (C=O, ketone), 1746 (C=O, ester), 1608, 1496 (arom ring vibr), 1525, 1350 ($NO_2$), 1252 (CO), 858 $cm^{-1}$ ($C_6H_4$ wagg); $^1H$ NMR ($CDCl_3$) $\delta$ 1.42 (s, 2 $CH_3$), 1.55, 1.71 (2s, 2 $CH_3$), 3.0–3.5 (m, 6-$H_2$), 3.66 (s, $OCH_3$), 4.22 (dd, $J$ = 8.6 and 9.5 Hz, 7-H), 7.65, 8.12 (AA′BB′, $C_6H_4$). Anal. Calcd for $C_{20}H_{22}N_2O_5S$: C, 59.68; H, 5.51; N, 6.96; S, 7.97. Found: C, 59.92; H, 5.51; N, 6.86; S, 8.01.

b. The reaction in THF and 3 vol % water provided 55% **17d** ($\delta$ 3.66) and 35% of lactams **19dA,B** ($\delta$ 3.66); $ClCH{=}CCl_2$ was the weighed standard in the $^1H$ NMR analysis. In the PTLC ($SiO_2$, $CH_2Cl_2$/acetone 95:5), thiolane **17d** (43% isolated) was followed by **19dA** (2%) and **19dB** (18%).

Methyl 10-aza-1,1,3,3-tetramethyl-2,9-dioxo-7-(*p*-nitrophenyl)-5-thiaspiro[3.6]decane-8-carboxylate (**19dA**): colorless needles, mp 186–188 °C (ethanol); IR (KBr) 3421 (br, NH), 1785 (C=O, ketone), 1751 (C=O, ester), 1675 (amide I), 1605 (arom ring vibr), 1521, 1347 ($NO_2$), 1030 (CO), 855 ($C_6H_4$ wagg); $^1H$ NMR ($CDCl_3$) $\delta$ 1.38, 1.41, 1.45, 1.52 (4s, 4 $CH_3$), 2.75–4.2 (m, 6-$H_2$, 7-H), 3.62 (s, $OCH_3$), 4.34 (d, $J$ = 6.0 Hz, 8-H), 7.53 and 8.05 (AA′BB′, $C_6H_4$). Anal. Calcd for $C_{20}H_{24}N_2O_6S$: C, 57.12; H, 5.75; N, 6.66. Found: C, 57.20; H, 5.78; N, 6.48.

Isomer **19dB**: mp 199–200 °C (ethyl acetate); IR (KBr) 3400 (br, NH), 1784 (C=O, ketone), 1755 (C=O, ester), 1605, 1598 (arom ring vibr), 1521, 1368 ($NO_2$), 1286, 1212, 1157, 1029 (CO, CN), 856 $cm^{-1}$ ($C_6H_4$ wagg); $^1H$ NMR ($CDCl_3$) $\delta$ 1.35 (s, 2 $CH_3$), 1.50, 1.60 (2s, 2 $CH_3$), 2.4–3.7 (m, 6-$H_2$, 7-H), 3.61 (s, $OCH_3$), 4.15 (d, $J$ = 10.8 Hz, 8-H), 6.15 (br, NH), 7.55, 8.12 (AA′BB′, $C_6H_4$). Anal. Calcd for $C_{20}H_{24}N_2O_6S$: C, 57.12; H, 5.75; N, 6.66; S, 7.62. Found: C, 57.41; H, 5.70; N, 6.66; S, 7.69.

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